

TREATMENT OF SPENT POT LINING BY CHEMICAL LEACHING USING NITRIC ACID FOR ENRICHMENT OF ITS FUEL VALUE AND OPTIMIZATION OF THE PROCESS PARAMETERS

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In

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Under the supervision of

Prof. Pradip Rath

Submitted by

Newton Bishoyi

Roll Number- 111CH0064



**DEPARTMENT OF CHEMICAL ENGINEERING,
NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA,**

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National Institute of Technology, Rourkela



CERTIFICATE

This is to certify that the project report entitled, “Treatment of Spent Pot Lining by Chemical Leaching Using Nitric Acid For Enrichment of Its Fuel Value And Optimization of The Process Parameters” submitted by Newton Bishoyi (111CH0064) in partial fulfilment for the requirements for an award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology Rourkela is prepared by him under my supervision and guidance and this work is not been submitted elsewhere for a degree.

Date:
Place: Rourkela

Prof. Pradip Rath
(Project Supervisor)
Department of Chemical Engineering,
NIT rourkela-769008

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Date:

Newton Bishoyi
Roll Number- 111CH0064

ABSTRACT

Over the years numerous methods have been suggested for treatment of Spent Pot Lining (SPL)- a waste produced from aluminum industries that has been declared as hazardous by the US Environmental Protection Agency. In this project chemical leaching treatment method was adopted and several process parameters and their dependency on each other were studied. SPL was subjected to caustic leaching followed by HNO_3 leaching at different temperature and liquid to solid ratio combinations. Again an optimized set of values was obtained via Taguchi method. The main objective of the optimization methodology was to determine the effect of acid concentration, alkali concentration, temperature and L/S ratio on the leaching percentage in terms of percentage contribution. Alkali concentration contributed 51.80% in the leaching process, whereas acid concentration contributed only 2.61 %. The maximum leaching percentage was found out to be 50.62% by Taguchi optimization. It was concluded that 2.5 M NaOH, 5 M HNO_3 concentration, 4.5 L/S ratio and temperature $75 \pm 1^\circ\text{C}$ was the best combination for the optimum leaching percentage for final treated SPL. The carbon percentage of SPL was increased from 33.27% to 87.31% as confirmed from the elemental composition obtained by Energy Dispersive X-ray spectroscopy. Again with the help of existing data, an extensive comparison was made to find out the best suitable acid out of HCl, HNO_3 , H_2SO_4 and HClO_4 for leaching process keeping L/S ratio constant. It was observed that at normal temperatures H_2SO_4 gave maximum leaching percentage for all values of alkali concentrations. But as temperature was increased from 25°C to 100°C , the leaching percentage obtained by all acids converged slowly to a constant range.

Keywords: Spent Pot Lining, Taguchi method, chemical leaching, optimization

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ABBREVIATIONS

ADJ.SS: Adjusted Sum of Squares

ADJ.MS: Adjusted Mean Squares

Al₂O₃: ALUMINA (Corundum)

Al(OH)₃: Gibbsite (Aluminum Hydroxide)

ANOVA: Analysis of Variance

C: CARBON

CaF₂: Fluorite (Calcium Fluoride)

CHNS: Carbon, Hydrogen, Nitrogen, Sulfur

DOE: Design of Experiment

EPA: Environmental Protection Agency

EDX: Energy-Dispersive X-ray Spectroscopy

FESEM: Field Emission Scanning Electron Microscope

L/S: Liquid to Solid

M: Molarity

Na₃AlF₆: Cryolite

NaAl₁₁O₁₇: Diaoyudaoite (Sodium Aluminum Oxide)

NaF: Villiaumite (Sodium Fluoride)

SEM: Scanning Electron Microscope

SEQ. SS: Sequential Sum of Squares

SiO₂: Quartz

SPL: Spent Pot Lining

S/N RATIO: Signal to Noise Ratio

XRD: X-Ray Diffraction

CHAPTER 1:

INTRODUCTION

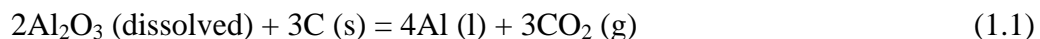
1.1. ALUMINUM ELECTROLYSIS AND CELL DESIGN

The most abundant metal in earth's crust is Aluminum which makes up about 8% by weight of the earth's solid surface. Aluminum metal is chemically so reactive that its native specimens are rare. Instead, it is found combined in over 270 different minerals. Two process steps are adopted for the aluminum production. The primary procedure step includes the refining of the crude material bauxite (mineral), which contains 30-60 % alumina (Al_2O_3) to immaculate alumina (Al_2O_3). This is known as the Bayer methodology (1887) which was proposed by a Austrian scientific expert Karl Joseph Bayer (1847-1904). In the second step, alumina is electrochemically reduced by affecting electrical current. Aluminum can't be produced by the electrolysis of the dissolved solution of an aluminum salt because of the high reactivity of it. In 1886 an American exploratory scientist Charles Martin Hall and a Frenchman Paul Heroult unreservedly discovered the process of making aluminum electrolytically which was renamed after them as Hall-Heroult process. The Hall-Héroult process is the only industry oriented effective technique to produce essential aluminum. Amid the most recent decades expanding demand of aluminum metal has convinced aluminum industries to utilize more effective cells. It has constrained the industries to utilize solid materials in the cells. The carbon cathode is a standout amongst the most vital parts in the cell, which decides the service life of the aluminum reduction cells¹.

Generation of aluminum from alumina (Al_2O_3) is inconceivable by the electrolysis of aluminum salt dissolved in water on the grounds that hydronium particles promptly oxidize basic aluminum. As the temperature required to melt aluminum oxide is above 2000 °C, for electrolysis of alumina a molten aluminum salt can be utilized. The innovators of this process, Hall and Héroult found independently of one another the electrochemical methodology to reduce alumina to aluminum metal². In the Hall- Héroult procedure, alumina dissolved in cryolite (Na_3AlF_6) reacts electrochemically to produce pure aluminum and carbon dioxide in between a carbon anode that is expended and a carbon cathode at around 960 °C³. Composition of the bath

is a compromise between electrical conductivity, current efficiency, alumina and metal solubility, density and vapor pressure⁶.

The overall cell reaction is given in Eq. (1.1), and a schematic drawing of a cell is shown in Figure 1.1.



Mechanically, the electrolyte is a melt, in light of cryolite, which contains fractions of AlF_3 and some different additives (CaF_2 , LiF) to change the essential properties of the bath, for example, the aluminum solubility, melting point and electrical conductivity⁴.

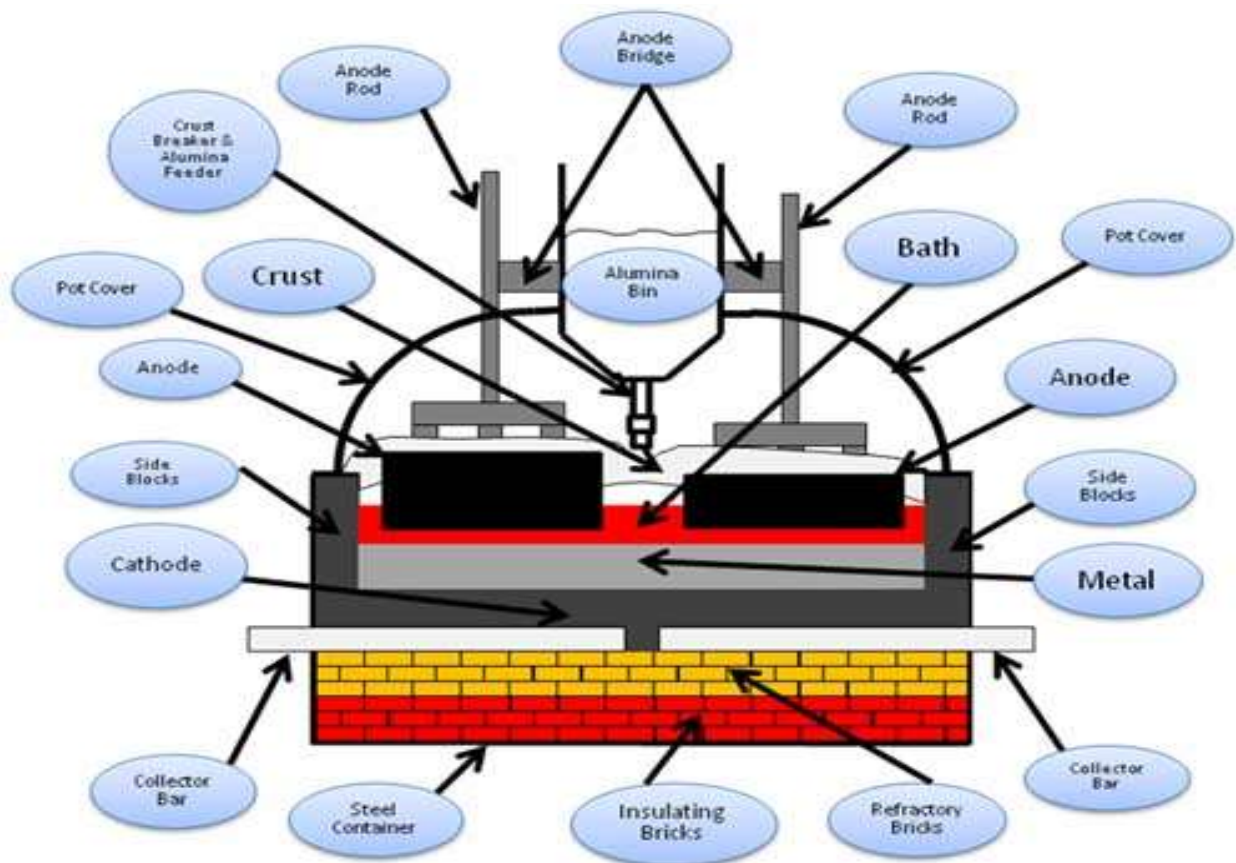


Figure:1.1 Schematic diagram of Hall-Heroult cell

Alumina is fed into the cell routinely amid the procedure and aluminum is generated constantly on the cathode surface. Alumina (Al_2O_3) is sustained to the bath through punched openings in the crust. This is carried out by point feeders in 1 to 2 kg per doses at each 1 to 2 minutes interim⁶. Alumina concentration and its cautious control are of crucial significance. High feeding rate may prompt formation of "sludge" or "muck" of undissolved alumina/bath. This leads the mixture of bath and undissolved alumina to sink down due to high density and thereby making it hard to evacuate. Despite of it, low alumina content may lead to the purported anode effect, which intrudes on the ordinary anode process by a sudden increment in cell voltage and a steep rise in bath temperature⁷. Due to anode effect harmful greenhouse gases such as perfluorocarbon gases are generated⁸. Preferably more than one anode are dipped into the molten electrolyte bath. The anode carbon reacts with oxygen from the alumina electrochemically and gets gradually consumed by forming carbon dioxide (CO_2)³.

There are two industrial anode designs used in modern aluminum cells: The prebaked and the continuous self-baking Soderberg anode⁸. Out of these, Soderberg is an outdated technology and supplanted effectively by the prebaked anode. The former one supposedly consumes less energy and maintains minimal degree of emissions. Therefore, in this thesis the prebaked technology, which utilizes various anodes as a part of each cell, is more highlighted. These anodes are made of molded blocks of coal tar pitch and petroleum coke which are heated in particular furnaces and afterward set in the cells³. Anodes function as current suppliers with in the cell. A general highlight of the Hall-Heroult process is that the anodes are devoured. While the anode is expended to ensure a consistent entomb polar distance (distance between the cathode and anode), it's height needs to be balanced.

In Hall- Héroult cell, molten aluminum is the acting electrochemical cathode, where the cathodic reaction occurs. However the whole assembly is called the cathode, i.e. molten aluminum, carbon blocks, baked ramming paste, refractory and insulation, collector bars and steel shell⁵. The cathode lining can be further arranged into "carbon and non-carbon lining" and additionally "bottom and side lining". The non-carbon gathering contains thick refractories, (for example, high alumina and chamotte) and thermal insulation bricks such as diatomaceous, vermiculite, calcium silica or others. They are put between the carbon blocks and the steel shell to shape the establishment of the cell superstructure. The carbon part of the covering comprises fundamentally of silicon carbide sidewall blocks and prebaked carbon base blocks. The carbon

cathode does not partake in the reaction, however serves as a holder and electrical connection with the aluminum pad.

1.2. THE CATHODE WEAR PHENOMENA:

Cathode wear is one of the essential factors deciding the service life of Hall- Héroult aluminum electrolysis cells. Wear is the phenomena of net expulsion of material from a surface⁹. The primary cause behind the shutdown of electrochemical cells in the aluminum industry is the cathode wear. The carbon block is worn ceaselessly amid operation until the steel collector bars become exposed to the aluminum pad. At that point the cell must shut down because a remarkable amount of iron content starts to appear in the produced aluminum¹⁰. On the first hand, the phenomenon is related to the cathodes having high electrical conductivity, where the current density of the carbon is also non-uniform across its surface up to some extent. Just about the whole current passes through a narrow zone located along the periphery. It seems to be generally agreed that in some way or another the wear is related to the current density, yet no sustainable mechanism has been discovered¹¹.

Anthracite, graphitic material and graphitized material are the three carbon sources from which carbon cathode as prebaked blocks is produced. However, Cokes are generally poorly ordered material which may contain impurities. As hydrogen atoms are bonded to the peripheral carbon atoms, when heat-treated, the hydrogen and volatiles get slowly removed from the structure. The layers become more and more parallel and the distance between the layers decreases. A further rise in temperature (up to 3273 K) can lead to crystallite growth till the material becomes mostly graphitic⁵.

Amid the most recent decades, the substitution of anthracitic with graphitized carbon materials has been a huge accomplishment because of the decrease of the electrical resistivity and a lower aggregate expansion⁸. The four primary classes of cathode blocks for aluminum reduction cells are anthracitic, semi-graphitic, semi-graphitized and graphitized, where the graphitic character is increased in the written sequence. In the last 10-20 years critical changes from using just

anthracitic carbon to semi-graphitic, semi-graphitized or graphitized materials have occurred. Graphite having higher thermal and electrical conductivities is less vulnerable to sodium penetration than anthracitic carbon. Graphite additionally has a higher thermal shock resistance, which is favorable during preheating and startup of new cells^{4,5,8}.

In the meantime as the thermal conductivity of the cathode has enhanced, the isotherms begin shifting downwards in the lining. Beneath the carbon blocks refractory layers are introduced to keep up the required heat balance and to protect the insulation blocks underneath against higher temperatures and chemical attack⁷. The most widely recognized refractory materials are found in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ framework. These materials are called alumino-silicates which can be distinguished by their alumina content¹². Alumino-silicates have been and still are the favored refractory materials because of light weight, accessibility, noble performance and moderate expenses^{4,6,8}. The refractory material can't totally withstand the constant chemical attack brought on by the uptake of sodium and electrolyte/bath segments. Amid operation sodium permeates through the carbon cathode blocks which cause swelling and cracking. Cracks are one of the principle explanations behind premature cathode failure^{6,7}.

Underneath the carbon block sodium and bath components start to deteriorate the refractory lining^{12,13,14,15}. This leads to significant mineralogical transformations in the material. Hence the material performance changes over time, resulting in increased heat loss through the cathode lining, rise in mechanical stresses (due to swelling) and in the worst case it causes a complete pot failure^{17,7}. During industrial electrolysis of aluminum the wear rate of the cathode carbon is in the range of 2-6 cm/year⁴. This equals 0.05-0.16 mm/day. Since these material and operating expenses have a significant effect on the production cost, the aluminum producers are aiming to decrease the number of unscheduled shutdowns and increase the average service life span to about 3000-4000 days^{7,18}. The cathode, after continuous operations around variable period of time (1100-3000 days), is discarded and replaced with new one. The dismantled cathode or Spent Pot Lining (SPL) is a hazardous waste comprising of 20 wt.% fluoride and 1 wt.% cyanide which is a major environmental concern¹⁹.

1.3. PURPOSE OF THE PROJECT WORK:

SPL is toxic in nature as it contains leachable fluorides and cyanides. SPL is also considered as corrosive due to the presence of alkali metals and oxides which react with water thereby producing inflammable, toxic and explosive gases. The sole purpose of this thesis comes from the importance of the treatment of Spent Pot Lining (SPL). Basically three different methods as stated below are available for treatment of SPL in a commercial process^{19,20,21}. They are

- Density separation method
- Hydrometallurgical process
- Pyrometallurgical process

Moreover none of these above methods were widely accepted due to the following reasons.

- None of the methods has less number of steps to minimize cost.
- Very low grinding index of SPL (i.e. 22) which implies a high cost for milling and grinding.
- It was practically impossible to recover valuable materials like graphite and fluoride in form of smelter grade raw materials.
- Cyanide removal and elimination was not noteworthy.
- Environmental concerns arising out of disposal of treated SPL.

This thesis gives an insight about the adapted optimization techniques to monitor the anticipated process parameters and also provide different approaches in the treatment as well as comparison of treatment processes. Another scope of this study is the possible use of treated SPL as a carbon rich fuel. Again a comparison of leach ability of various acids using the existing data has to be done.

1.4. ORGANIZATION OF THE THESIS

The thesis is organized in five chapters. The layout of the chapters is as follows:

- *Chapter-1* is an introductory chapter in the field of aluminum electrolysis and cathode lining.

- *Chapter-2* contains apposite literature review on Spent Pot Lining (SPL). It highlights production of SPL, several treatment methods that have been sprang up till date to recover and recycle the valuable components from SPL.
- *Chapter-3* describes about the materials and instrumentation details as well as the brief introduction of adopted optimization technique for the treatment of SPL.
- *Chapter-4* represents the results and discussion extensively obtained from the experiments.
- *Chapter-5* concludes the findings and future aspects of this study.

Evidently, this thesis highlights the use of diverse materials for the treatment of SPL additionally its enrichment and utilization. As specified before, these materials were chosen on the premise of their applications. The process parameters were optimized using standard techniques and correlated with the experimental findings accordingly.

CHAPTER 2:

LITERATURE REVIEW

With the developing Industrial Revolution, humans were able to advance further into the 21st century. Technical innovation developed ominously, science achieved remarkable progress and the manufacturing age came into picture. With these changes in industrial and economical scope came one more impact, industrial hazards and contamination because of it. With subsequent advance in industrialization, many hazardous wastes become possibly the most important factor which has an impeding impact on nature bringing on a significant concern among the industry and society. Aluminum industry is regarded as one of the swiftly growing industries in which industrial wastes formed such as Spent Pot Lining (SPL) are of foremost environmental concern. In this part the thesis, generation of Spent Pot Lining (SPL) and different treatment methodologies are specified.

2.1 SPENT POT LINING: FACTS AND TRIVIA

2.1.1 Visual Appearance Of Spent Pot Lining And Its Composition:

During degradation significant mineralogical transformations in the refractory lining have been shown to occur^{8,12}. The texture and appearance of the reaction section in SPL may be varied from cell to cell as it depends on cell age and operational constraints. However, the secondary phases appear to be the equivalent, nevertheless the amount varies quite substantially. Naturally, the SPL comprises of integral compacted insulation bricks underneath reacted refractories. As shown in Fig. 2.1, in shutdown cells two layers in the spent refractory lining are visually distinct.



Figure 2.1: Different layers in a cathode bottom lining after 1500 days in operation⁴⁴

The upper part (towards the carbon block) is inhomogeneous, white greyish in colour and named as "build-up". Excluding trivial amounts of phases like aluminium (Al), Al_4C_3 , FeSi, and Fe-Al alloys it has been predicted that mostly NaF, Na_3AlF_6 and $\beta\text{-Al}_2\text{O}_3$ are present. The crystalline like structure of this layer is filled with voids and gaps. The appearance of the subsequent part named "reacted part" is black and dense. In this area, large amounts of nepheline (NaAlSiO_4) and glassy-phase have been found. The glassy-phase is assumed to be structurally similar to albite ($\text{NaAlSi}_3\text{O}_8$)⁸. The juncture between the reacted part and integral firebrick is a sharp interface, named "reaction front".

The estimation of temperatures in the lining during operation is based on calculations using the properties of unreacted materials, as shown in Fig. 2.2.

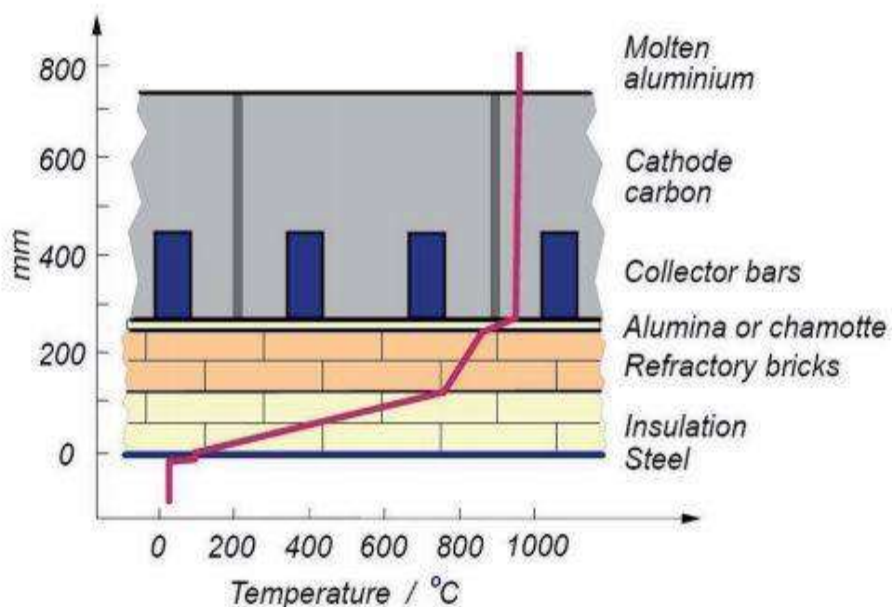


Figure 2.2: Schematic cross-section through a common bottom lining showing temperature gradient

The figure above also visualizes the temperature gradient in the lining, designed with data and dimensions as for new-fangled material⁴⁵.

Diversified opinions are drawn through various research works regarding the amount of production of SPL by a cell per tonne of aluminum produced. Typically in Soderbergs production rate is 35kg/tonne, end to end and in case of prebakes it is 20-28 kg SPL/tonne. The failed cell lining is either demolished and repaired in the cell rooms or removed from the cell rooms. The shell and lining are taken to a specialized demolition and relining facility. The resulting material is called Spent Pot Lining. The portion above the collector bars contains mainly carbon [amorphous, varying proportions of graphite (30–100%) and is often referred to as the first cut]. The fraction below the collector bar (second cut) is essentially composed of refractory bricks (insulating and firebricks). Several factors contribute to the variation in composition found in the literatures for SPL. In addition to the initial components used to build a new cell lining, which is different for each technology, when the pots are taken offline, some bath and frozen aluminum will remain inside the pot and will end up, to a variable extent mixed with the original cell lining components. The amount of bath and frozen aluminum will depend on the dismantling procedures. The composition will also depend on how long the pot is operated. The sodium and NaF will have diffused deeper inside the lining for pots that have

operated longer, increasing the sodium and fluoride content in SPL. This will also depend on the type of brick.

Table 2.1 gives the composition of the SPL for three different technologies. The reference to this composition was a fused specimen of a 250-ton silo full with -300 mesh SPL. The sample is for joint first and second cut. Table 2.1 presents that the fluoride ion content and the cyanide concentration are also contingent on the technology and several different factors delineated above. Type A and type B are two types of recent prebakes. The fluoride and cyanide content are considered as the most critical toxic ingredients and thereby demands treatment process to make the byproducts from the industry harmless and contamination free. In the prospect that the first and second cut can be separated during dismantling the pots, the composition would vary with higher fluorides, sodium, and cyanides in the first cut.

Table 2.1: Composition of SPL for different technologies²¹

Elements	A type	B type	Soderberg	Major phases
Fluorides (wt. %)	10.9	15.5	18	Na ₃ AlF ₆ , NaF, CaF ₂
Cyanides (ppm)	680	4480	1040	NaCN, NaFe(CN) ₆ , Na ₃ FeCN ₆
Ratio (HCN/Total)	2.7	1.9	3.4	
Aluminum total (wt. %)	13.6	11	12.5	Al ₂ O ₃ , NaAl ₁₁ O ₁₇
Carbon (wt. %)	50.2	45.5	38.4	Graphite
Sodium (wt. %)	12.5	16.3	14.3	Na ₃ AlF ₆ , NaF
Al metal (wt. %)	1	1	1.9	Metal
Calcium (wt. %)	1.3	2.4	2.4	CaF ₂
Iron (wt. %)	2.9	3.1	4.3	Fe ₂ O ₃
Lithium (wt. %)	0.03	0.03	0.6	Li ₃ AlF ₆ , LiF
Titanium (wt. %)	0.23	0.24	0.15	TiB ₂
Magnesium (wt. %)	0.23	0.09	0.2	MgF ₂

2.1.2 Spent Pot Lining Reactivity and Toxicity

Because SPL was submitted to high temperatures, some water reactive chemicals were generated during the cell life. So, in addition to a variety of fluoride, sodium, and aluminum compounds, SPL also contains cyanides (caused by ingress of air through the collector bars), metals (Al, Li, and Na), reactive metal oxides (Na_2O), nitrides, and carbides¹. These different compounds will react with moisture and produce NaOH , H_2 , C_2H_4 , and NH_3 . In the past, the SPL water reactivity was used to break loose the lining by soaking the complete cell in water. However, because of health, safety and environmental (HSE)² concerns, this practice is now abandoned, and today the lining is removed dry. The active nature of the material makes it:

1. Toxic – Because of fluoride and cyanide compounds that can be leached in water.
2. Corrosive - Because of high pH due to alkali metals and oxides.
3. Highly reactive with water - Because of production of inflammable and explosive gases

The above mentioned properties make SPL demand for a vigorous treatment method. Also, the toxic, corrosive, and reactive nature of the material signifies that its handling, transportation in closed cargos, and storage in dump sites should be avoided. Inter-country hazardous waste transfer is governed by convention²³.

2.1.3 Processing Options for Spent Pot Lining

Since the late 1970s and 1990s, the aluminum industry's target was to improve an economic procedure to recycle the heterogeneous SPL materials back into the aluminum industry. There are many procedures various industries and lab researchers have suggested from a technical point of view. But an economical optimized model has not been made progress till now. Several possibilities can be taken into account for SPL treatment. But the intricacy of the treatment process depends on how practically valuable components can be recovered from SPL. For extracting out the toxic content from SPL or to make recycling of it possible, various approaches have been discussed. Pyrometallurgy or hydrometallurgy can be considered and in fact, just about any combinations of various possibilities have been discussed over the years by private or public research groups. The most advanced processes and their present status are summarized in

this thesis. The most challenging factor for the total recycling of SPL is its composition which is heterogeneous. Few industrial pyrometallurgical processes are capable of using the SPL as produced. The cement industry is one of the first industries that started using SPL, and still uses it in few countries. Nevertheless, there are bound restrictions on the sodium and fluoride content in the final product, which confines the quantity of SPL that can be supplied to a cement kiln. This is for the high sodium content in SPL which is shown in Table 2.1. The other industries that use SPL are the mineral, wool, iron and steel industries. All hydrometallurgical approaches intended at total recycling of SPL demands a separation of the key fractions—carbon, brick, and fluorides. Partial recycle and disposal of SPL is less rigorous. Subjected to the economics, some specific components can be targeted for recycling. For example, during the time that the industry operated smelters with wet effluent treatment centers, cryolite recovery could be achieved. Another example of partial recycling was operated for some time at Alcan's Kitimat smelter with the Williams process where the lining carbon blocks were autoclaved with steam and the recovered hydrated carbon (HRC) was used in the monolithic of the next generation of cells. The rest part of the lining was landfilled. Safe disposal of SPL needs some kind of treatment to alleviate the leachable fluoride and to decompose all water reactive compounds and the cyanides. Indeed, each plant must choose between the alternatives allowed by its legislation. This has prompted to several kinds of solutions.

2.1.4 Environmental Legislation Considerations

Previously SPL was being classified as a mining or industrial waste for which disposal was not a major concern. SPL was disposed of in lined or unlined landfill locations. As SPL became classified as a hazardous waste in 1988 in the United States⁵ and a special waste in Canada, many landfilled sites required renovations. For industries dispensing hazardous wastes, environmental regulations are stricter, and it became more difficult for the cement and steel industries to accept unprocessed SPL. This meant partial or total detoxification had to be done before reusing the SPL by a third party.

2.1.5 Current Storage of SPL

How SPL is stored or processed depends on the classification of SPL under each country's national and provincial (state) legislation, i.e., industrial, special, or hazardous waste. Based on current production levels, the authors estimate that a significant amount of SPL more than >50% is still stored in buildings in lined and unlined sites, waiting for treatment. This estimate excludes

China. The percentage would rise to over 75% if China were included. What could be considered as a passive treatment was done in Norway and Iceland where SPL has been deposited on the seashore allowing sea leaching of soluble components. The leachable fluorides present in SPL will react with the calcium ions in seawater to form a stable calcium fluoride. An extensive research by the University of Iceland did not indicate that the dumping pits had detrimental effects on shore communities.

2.2. TREATMENT AND RECOVERY PROCESSES

Over the years many processes have been developed, out of which hydrometallurgical or pyrometallurgical processes found to be suitable.

2.2.1 Lab scale improvements:

Various researchers have examined to mitigate the harmful effect of SPL by employing different approaches.

2.2.1 a) Hydrometallurgical approach

The Melbourne Process, one of the primary and successful laboratory methods has already been implemented on a pilot plant. Cyanide is adequately removed in the water wash stage and fluoride is recovered as CaF_2 . The acid washes remove the rest of the fluoride and a significant quantity of this is recovered as AlF_3 . The process flow diagram is as shown below:

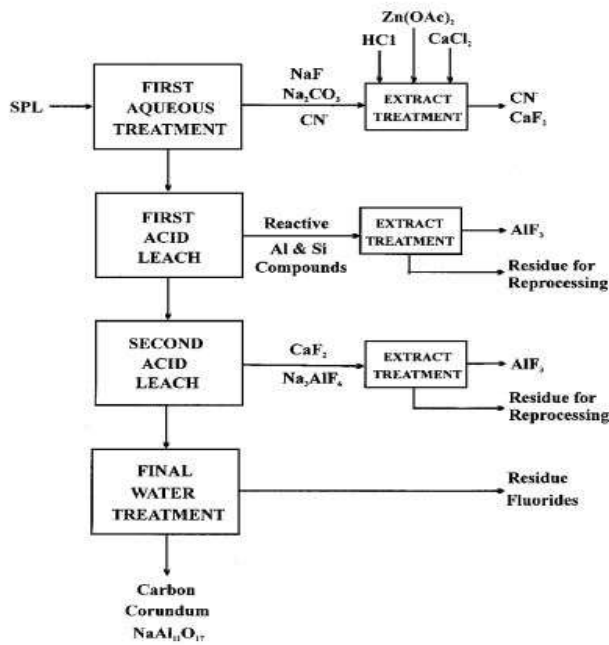


Figure 2.3: Schematic flow diagram of the Melbourne Process

In the year 1999 Baranovskii et al. proposed a method for recovery of soda and potash by mixing crushed first cut SPL limestone and then adding this mixture to an aqueous slurry²⁰. A couple of years later separation of aluminum electrolysis carbon froth and spent pot lining by froth flotation technique was applied by Lu et al. Chinese researcher Zhao²⁴ suggested an integrated method for recovering waste aluminum reduction cell lining, which is characterized by the following steps:

- i) Drying aluminum reduction cell lining of waste processed into powder;
- ii) Injecting water into the concentrated sulfuric acid solution, so that it is diluted and heated by hot spent aluminum reduction cell lining;
- iii) The hydrogen fluoride gas generated by the reaction rinsed repeatedly using water absorption process and thereby recycling industrial hydrofluoric acid;

Until 2002, no researcher has brought out pH of Spent Pot Lining as a significant parameter which said to affect the dissolved fluoride content. As proposed by Silveira et al.^{25,26}, the leaching behavior of SPL was studied and it was found that total dissolved fluoride at pH 12 and at pH 5 was 6.45-9.39% and 0.26-3.46% respectively. Lisbona and Steel²⁸ implemented a fluoride extraction method by using 0.34 Al^{3+} solution at 25°C for 24 h. In the pH range 4.5-5.5, selective precipitation of fluoride as an aluminum hydroxyfluoride hydrate product was achieved by neutralization. It is again found that higher pH leads to co-precipitation of hydrolyzed sodium fluoroaluminates. Unlike fluoride removal NaF and Na_2CO_3 content from SPL could easily be removed by water washing of SPL. Precipitated fluorides in a form that can be recycled back into the pot have been studied by manipulating solution equilibria²⁹.

Recently in the year 2012, a two-step alkaline-acidic leaching process was conducted by Zhongning et al.²⁷ to separate the cryolite from spent pot lining and to purify the carbon. The influencing factors of temperature, time, and the ratio of liquid to solid in alkaline and acidic leaching were investigated. The results showed that the recovery of soluble compounds of Na_3AlF_6 and Al_2O_3 dissolving into the solution during the NaOH leaching was 65.0%, and the purity of carbon reached 72.7%. During the next step of HCl leaching, the recovery of soluble compounds of CaF_2 and $\text{NaAl}_{11}\text{O}_{17}$ dissolving into the HCl solution was 96.2%, and the carbon

purity increased up to 96.4%. By mixing the acidic leaching solution and the alkaline leaching solution, the cryolite precipitated under suitable conditions of pH value 9 at 70°C for 2 h. The cryolite precipitating rate was found to be 95.6% and the purity of Na₃AlF₆ obtained was 96.4%.

2.2.1 b) Pyrometallurgical Approach:

V. A. Utkov et al.^{30,31} suggested neutralization of water soluble NaCN by treating the carbon rich part with an FeSO₄. Heating of second cut SPL up to more than 750°C to remove molten and volatile impurities was a noble initiative as described by Oliveira et al.³². Courbariaux et al.^{33,34} demonstrated another innovative yet restricted method of treatment of crushed SPL in a circulating fluid bed. The effect of the residence time on the concentration of cyanides, the effect of additives on the agglomeration properties of Spent Pot Liners were determined along with the leaching properties of the treated waste. In this study, conditions of temperatures had also been examined, which lower the agglomeration risks and maximize the destruction of cyanides. Fluorides available in Spent Pot Linings were found to have a general composition of NaF. During combustion, Spent Pot Linings react with oxygen according to the reaction described in equation:



According to the findings by Courbariaux et al., during the combustion, fluorides can undergo reactions according to three possible paths: It may react with steam at high temperatures:



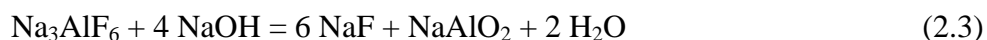
Again destabilization during the combustion may cause fluorides become more easily leachable. On the other hand there can be situations when fluorides content remain attached to the treated residues and are not available for leaching.

Heating of crushed SPL mix to about 1000°C and adding lime to oxidize cyanides followed by binding the fluoride was another approach suggested by Li and Chen^{20,26} who also analyzed chemical stability of the fluorides in the SPL. Presence of graphite and sodium in SPL makes it sticky, slippery and difficult to crush. Blinov et al carried out a pyrohydrolysis process to recover fluorine as HF and manifested possible use of carbon rich part in pig Iron manufacture.

2.2.2 Industrial scale improvements

2.2.2 a) Hydrometallurgical Processes

Hydrometallurgical treatment of SPL can be conducted in water, acid, or basic solution,^{35,36} but only the caustic conditions can lead to a total extraction of the leachable fluorides present with the SPL. Also, as cryolite Na_3AlF_6 is not soluble in water or in acid solution, the residual solids after treatment under those conditions will always exceed the 150 ppm level of leachable fluorides due to the presence of cryolite. Thus, even if some acid leaching of SPL have been proposed, most of the hydrometallurgical studies were done under caustic conditions. When considering a caustic leaching of Spent Pot Lining, two options are possible: a concentrated caustic leaching or a low caustic leaching (LCL) step⁴³. These two options give totally different processes mainly due to the solubility of sodium fluoride (NaF) and sodium aluminate (NaAlO_2) in caustic obtained from the dissolution of the cryolite (Na_3AlF_6) in caustic.



After the solid liquid separation of the caustic liquor, the NaF can be recovered by evaporating the caustic solution. This method was adapted by Rio Tinto Alcan (RTA)^{37,38}.

2.2.2 b) Pyrometallurgy Approach

Regain³⁸ in NSW Australia operates a low-temperature process for the destruction of simple cyanides to deactivate SPL (carbides, nitrides, etc.). Alcoa (Reynolds) Gum Springs process³⁹ incorporates destroying simple and complex cyanides in a rotary kiln at 1000°C and creating industrial waste for road aggregates. The process produces 2.5 tonnes of waste per tonne of SPL processed. The process produces a product that met the USAEPA (ACID) leachate tests but contained soluble caustic components and should be landfilled dry at a hazardous waste sites. RT (Comalco) COMTOR⁴⁰ method was a slight modification to Reynolds process. In this process the residue is leached with lime to produce a Bayer-type liquor and kiln-grade spar for the cement industry. The process produces a soluble caustic that can be recycled in a Bayer plant (QAL alumina plant) and the residue can be used as feedstock for a local cement kiln. The process was subsequently simplified by omitting the leaching step and creating a dry process. Similarly Oremet Process was responsible for producing a reusable industrial waste (glass frit)

for the glass industry and the HF gas was collected in a dry scrubber. A co-product containing a high concentration of fluorides (NaF) was used in the steel industry.

2.3 CONCLUSION AND PROPOSED EXPERIMENTAL WORK

The review of literatures in this chapter confirms that most of the treatment processes are optimized by conventional ways by using any of the specific optimization techniques. The new approaches of treatment with various other acids need to be studied as well as a comparison between them is the one of the main objectives of this project. The treatment of SPL is considered to be one of the biggest challenges due to presence of highly leachable fluoride and cyanide content.

However, physical separation method is difficult to improve the carbon purity and recovery efficiency of the leachable substance. For thermal treatment, the common way is to burn the SPL. Although the SPL is decomposed, some waste in SPL transfers into the refractory components, and the fluoride is recovered as a gaseous HF effluent which can be absorbed with smelter grade Al_2O_3 ⁴¹, while the carbon is burnt for boiler heating. This thermal treatment is complicated in operation and the valuable source of carbon is not reused.

In addition, the chemical leaching can leach the soluble compounds from the SPL by using NaOH or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ^{42,43}. Because of the low reaction rate, the approach for treating Na_3AlF_6 and CaF_2 using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ takes long time of 24 h at 25 °C²¹, which is not productive and very costly. However, the NaOH leaching just takes 2 to 3 h and the leaching reagent is economical. Hence for the proposed experimental work NaOH has been chosen as the appropriate alkali.

Some of the specific objectives are as follows:

- Characterization of SPL material
- Treatment of SPL with HNO_3 for leaching of NaF, CaF_2 , $\text{Al}(\text{OH})_3$.
- Treatment of SPL with NaOH, for leaching of Na_3AlF_6 , Al_2O_3 , NaF, CaF_2 .
- Enrichment of the carbon percentage of SPL samples using leaching process.
- Optimization of process parameters using Taguchi design to check dependency of various process parameters.

CHAPTER 3:

MATERIALS AND METHODS

Process specifications and materials used have been discussed in this part of the thesis.

3.1. MATERIALS USED

3.1.1 Chemicals

In the experimental method whatever chemicals were used were of highest purity. These have been obtained from Merck. Acid and alkali solutions were prepared using de-ionized water.

Alkali used: NaOH

Acid used: HNO₃ (69% Assay)

Cleansing reagent used: Methanol

3.1.2 Instruments and glasswares

Borosil manufactured glasswares were used for the experiments. All the glasswares were cleaned first using methanol as cleaning reagent.

The glasswares and other tools necessary for the experiment are mentioned below:

- Conical flask (250 ml)
- Beaker (250 ml)
- Pipette (25 ml and 100 ml)
- Funnel
- Plastic airtight bottles
- Plastic Jar (20 ltr)
- Centrifuge tubes (2 ml)
- MN Filter Paper-640

3.2. METHODOLOGY

The complete methodology in a brief way can be represented as the process flow diagram shown in fig.

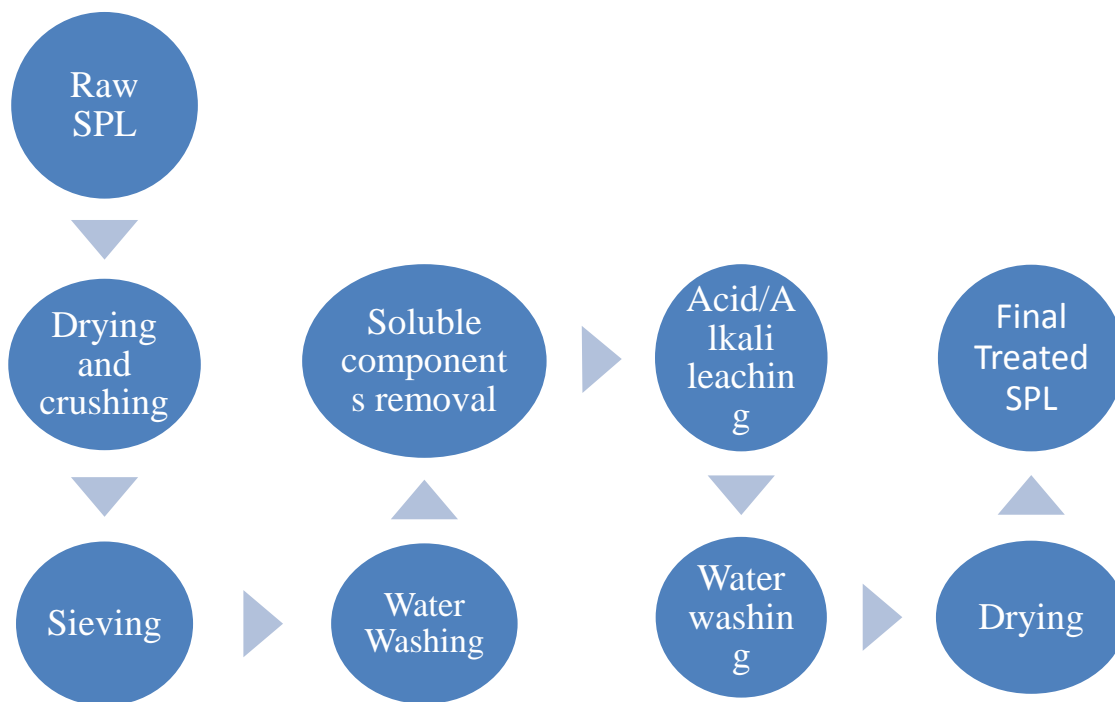


Figure 3.1: Schematic diagram of experimental process

3.2.1 Sample preparation

From Jharsuguda based Vedanta aluminum Ltd. the first cut Spent Pot Lining (SPL) sample was collected. In the first step, obtained SPL was put in oven for 4 hrs at $110 \pm 1^\circ\text{C}$ for drying purpose. The dried samples were then crushed in a ball mill. As particle size of 300 micron was desirable, sieving was done using a 52 BSS sieve.



Figure 3.2: Raw sample (Before grinding)



Figure 3.3: Orbital shaker arrangement



Figure 3.4: Water washed SPL & alkali mixture (Zoomed in view)



Figure 3.5: Actual diagram of experimental setup for higher temperature (Magnetic stirrer)

3.2.2 Water washing of Spent Pot Lining (SPL)

For water washing 5:1 L/S ratio was maintained to ensure maximum amount of fluoride removal. 50g of raw SPL was treated with 250ml of deionized water at $50 \pm 1^\circ\text{C}$ for a period of 4h in an orbital shaker at 120rpm. To decrease the pH of residues to a neutral range, SPL was thoroughly washed²⁶. This was done to eliminate the options of obtaining undesired products. Then using a Macherey-Nagel MN 640 filter paper all the compound those are soluble in water were removed. Once again the SPL residue collected on the filter paper was dried for 4hrs at $110 \pm 1^\circ\text{C}$. To obtain leaching percentage the following formula was used:

$$\% \text{ Leached} = [L_0 - L_e] / (L_0) \times 100$$

L_0 = initial weight of SPL before leaching

L_e = final weight of SPL after leaching

3.2.3 Alkali Leaching

The water washed SPL samples were subjected to alkali leaching followed by acid leaching according to the designed combinations. Each experimental step for alkali leaching was conducted with 6 g of sample weight. Then the treatments were done at 120 rpm and 4 h time either in orbital shaker (while dealing with temperatures at $25 \pm 1^\circ\text{C}$ & $50 \pm 1^\circ\text{C}$) or magnetic stirrer (for temperatures at $75 \pm 1^\circ\text{C}$ & $100 \pm 1^\circ\text{C}$). After each set of experiment, the leachates were filtered out by filter paper and the residue was put in a petri dish along with the filter paper and then dried in an oven for a period of 4 h at $110 \pm 1^\circ\text{C}$. The exact weight of the residue can be obtained by subtracting the weight of the filter paper. After alkali treatment is done, acid stock solutions at 4 different concentrations were prepared. 3 g from each of the alkali treated SPL samples were subjected to acid treatment. After each treatment, the pH of the residue²⁶ was brought down to neutral range as per standard methodology and then further characterization or treatment was done as per the requirement.

3.2.4 Design of Experiment by Taguchi design

The sole purpose of choosing the Taguchi design approach is that it helps in determining the effect of the each factor on various properties and the optimal condition of the factors. Undoubtedly, this is considered as one of the better and simple ways to optimize design for performance, cost and quality^{49,50}. Using analysis of variance (ANOVA) method the properties and their dependence on the factors defined can be checked. Orthogonal arrays can be implemented for the same experimental analysis. There are several pros of choosing the Taguchi optimization design over the optimization designs those are considered as conventional. Determination of the experiment concerned conditions becomes simpler with reduced variability. On the other hand using conventional optimization techniques, it is determined from measured values of significant characteristic properties. In Taguchi method the deviancy of desired value can be crosschecked by analyzing the signal/noise ratio. The experimental conditions at which signal to noise (S/N) ratio was appreciably higher and significant leaching percentage was

obtained were considered as the optimal conditions. The characteristics of variance were found to be inversely proportional to the S/N ratio. The specific range of parameters in the ‘4 level 4 factor’ design is given in the Table 3.2.

Independent variables	Levels			
Alkali concentration (M)	0.5	1.5	2.5	3.5
Acid concentration (M)	2.5	5	7.5	10
L/S ratio (cm ³ /g)	1.5	2.5	3.5	4.5
Temperature (°C)	25	50	75	100

Table 3.2: Ranges of experimental parameters for Taguchi design

Minitab worksheet was used to find out sixteen best possible combinations from the four levels and four factors as specified. The number of experiments required to conduct Taguchi design is quite less as compared to other designs of optimization available in the Minitab engineering software and it does not compromise on reliability.

3.3. CHARACTERIZATION OF SPENT POT LINING (SPL)

The SPL sample was characterized by several techniques to obtain the complete idea of all the components present in the SPL. The morphology of the structure was predicted by Scanning Electron Microscope (SEM) at 3 different magnifications 10 micron, 50 micron and 100 micron. Energy Dispersive X-Ray spectroscopy (EDX) was performed to find the elemental composition. The purpose and operating conditions of the experiments are highlighted in the Table 3.3. For XRD analysis the phases of all the materials were identified by the standard software provided with the XRD instrument i.e. “X’Pert Highscore” version 1.0b. The PDF2 database was used for the identification of particular component in the sample.

Table 3.3: Instruments used and purpose

Instrument	Make	Operation conditions or specification	Purpose
Analytical balance	Sartorius (BS223S)	0.001 kg - 0.1 kg	Measurement of weight
pH meter	Systronics (361)	Useful for pH range of 4.5 to 9.5	EPA Method analysis of crystalline sample
Incubator shaker	Environmental orbital Shaker	<ul style="list-style-type: none"> • Speed: 120 rotations per minute. • Temperature: $25 \pm 1^\circ\text{C}$ and $50 \pm 1^\circ\text{C}$. 	Quivering conical flasks to enhance leaching
Scanning Electron Microscope-Energy-dispersive X-ray spectroscopy	JEOL (JSM-6480 LV) and Nova NanoSEM 450 by BRUKER	<ul style="list-style-type: none"> • Maximum magnification range: up to 10000X • Resolution : $1\mu\text{m}$ • Everhardt Thornley detector (secondary electron) and backscattered detector at solid state. • X-Ray Analysis: Oxford Instruments ISIS 310 system with “windowless” detector. • Silicon detector with ATW model for light components. 	To analyze the refractory part and the graphitic part in the magnified image of the sample
CHNS analyzer	Elementar vario ElCube CHNSO.	<ul style="list-style-type: none"> • For measuring the content of nitrogen, hydrogen and Sulfur of the SPL sample • Initial wt.- per sample under 10mg 	To calculate elemental weight percentage and atomic percentage
X-ray diffraction analysis	Philips X'Pert X-ray diffractometer	<ul style="list-style-type: none"> • Cu $K\alpha$ radiation generated at 35 KV and 30 MA • Scattering angle 2θ ranging 5°-80° • Scanning rate of 3 degrees/minute 	For mineralogical analysis of SPL sample along various phase study.
Hot Air Oven	WEIBER	<ul style="list-style-type: none"> • Temperature: $110 \pm 1^\circ\text{C}$ • Time of operation: 4 h maximum 	For drying of samples
Magnetic Stirrer	Spinot-Tarson, Spectro	<ul style="list-style-type: none"> • Speed: 120 rpm • Temperature: 75 and $100 \pm 1^\circ\text{C}$. 	For Stirring at high temperatures
Oven and furnace	Weiber, Adco-electric furnace	<ul style="list-style-type: none"> • As per standards 	To perform proximate analysis ASTM-D-3172,3173,3174,3175

CHAPTER 4:

RESULTS AND DISCUSSIONS

Two approaches were adopted for treating water washed SPL. In the first part treatment with nitric acid was directly performed. The second part involved a two step leaching process in which the water washed sample underwent caustic leaching followed by nitric acid leaching. The parameters involved in the process were optimized by the use of Taguchi method. In the later part of the thesis elemental composition and carbon percentage of the raw sample, water washed sample, sample treated with alkali and the final treated sample were discussed. A comparison was again made using the preexisting data of various acids.

4.1. TAGUCHI APPROACH FOR OPTIMIZATION

The methodology of optimization was aimed at predicting the substantial effect of HNO_3 concentration, NaOH concentration, temperature & L/S on the primary leaching extent in form of percentage contribution. One of the most significant terms used in this approach “signal” can be considered as the desired value (mean) for the characteristics of the output. Similarly the undesirable value is typically represented as “noise” in the output. Hence the obtained S/N ratio is the ratio of the mean of the output to the standard deviation. In Taguchi method the S/N ratio is considered as a measure of the quality characteristic deviating from the desired value. The “larger is better” was selected out of various predefined set of mathematical constraints for calculating the optimum leaching percentage. The Signal to Noise (S/N) ratio Y was determined by using the following equation,

$$Y = -10 \log \sum_k^n \binom{n}{k} x_k^{-2} \quad (4.1)$$

Where the number of tests is n and x_k is the comparison variable in the k^{th} experiment.

Table 4.1: The experimental values for leaching percentage under different conditions

Sl No.	Alkali Conc. (M)	Acid Conc. (M)	L/S (cm ³ /g)	Temperature (degree C)	Leaching Percentage %	S/N Ratio
1	0.5	2.5	1.5	25	32.7	30.2910
2	1.5	7.5	4.5	25	40.5	32.0521
3	2.5	10	2.5	25	42.33	32.9300
4	3.5	5	3.5	25	49.88	32.8453
5	0.5	5	2.5	50	40.05	33.2816
6	1.5	10	3.5	50	50.62	33.9446
7	2.5	7.5	1.5	50	46.78	32.1491
8	3.5	2.5	4.5	50	50.1	33.0864
9	0.5	7.5	3.5	75	44.31	34.2294
10	1.5	2.5	2.5	75	46.14	34.0538
11	2.5	5	4.5	75	50.43	33.4012
12	3.5	10	1.5	75	48.47	32.5330
13	0.5	10	4.5	100	43.88	34.3368
14	1.5	5	1.5	100	49.8	33.9585
15	2.5	2.5	3.5	100	49.46	34.3033
16	3.5	7.5	2.5	100	49.9	33.7095

From the plot showing the important effects for S/N ratio and from the mathematical equation, it was observed that with the increment in the value of S/N ratio the leaching percentage variance around the desired value decreases. From Figure 4.1 it can be concluded that more the effect of the parameter was significant, the deviation from the horizontal line was more. As evident from the graph alkali concentration and temperature seemed to dominate over other parameters when S/N ratio was concerned. Moreover, the comparative significance among all the process parameters involved for calculation of leaching percentage was required to be known. This was done to maintain prominent accuracy so that the process parameter levels with optimum

combination could be achieved. The same procedure was clarified by the analysis of variance of S/N ratio.

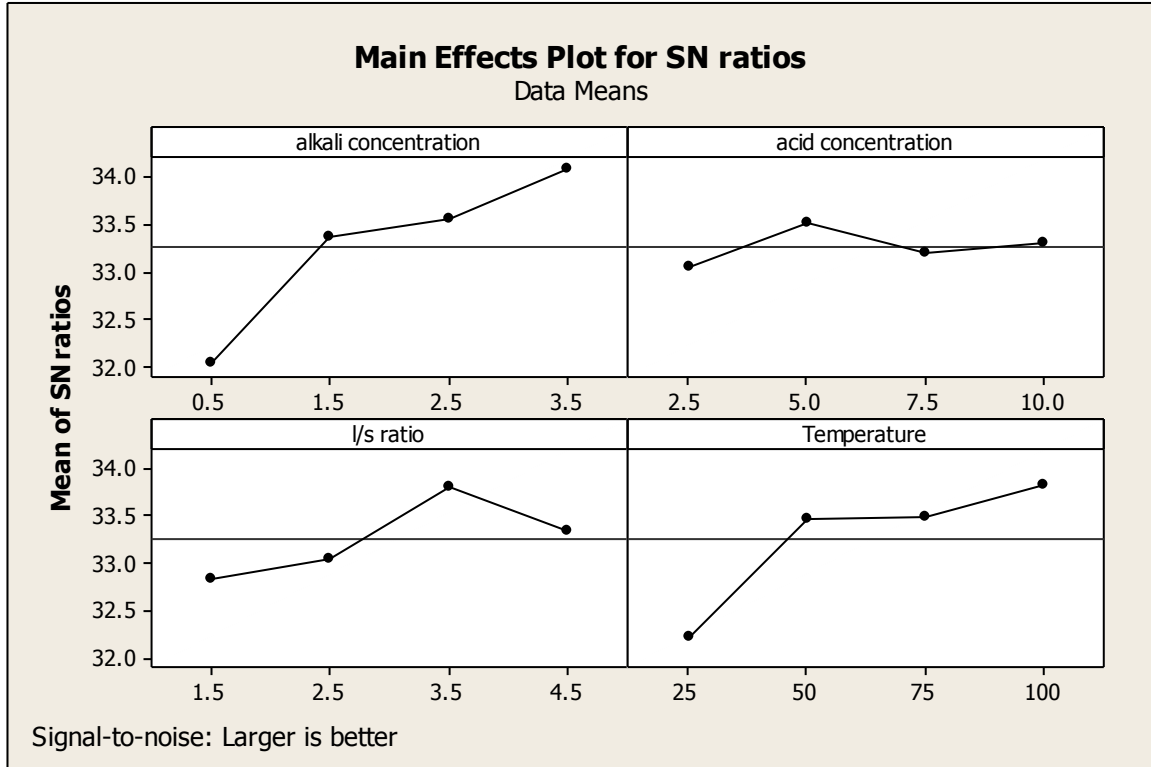


Figure 4.1: Main effect plot for the Taguchi optimization

4.1.1 Analysis of variance (ANOVA)

The process parameters can't be optimized alone just considering the various S/N ratio values alone. ANOVA can be better described as a set of statistical models that considers the changes between group means and the measures related to it. To determine the significant effect of few design parameters on the output characteristics was the primary cause for performing ANOVA. Dependency of all factors on the quality characteristic was predicted from the "Fisher (F)" test. The "F" value is the ratio of the mean of the squared deviations to the mean of squared errors. Usually, F value exceeding 4 is an indication that the specific design parameter disturbs the quality characteristics to a greater extent. In Table 4.2 the outcomes of analysis of variance (ANOVA) for percentage of leaching at several response conditions are shown. The optimal level of the design parameters was found out. Finally the changes in the quality characteristics at

the optimal design parameters combination were noted. At the optimal parameters the S/N ratios can be obtained and the various other associated parameters can be calculated by Eq. (4.1). One more fact that can be concluded is that the actual leaching percentage has a decent correspondence with the S/N ratio that has been shown in Table 4.1. From Table 4.2 it can be stated that, the alkali concentration and acid concentration were as the most and least significant parameters respectively among all the independent parameters based on F value.

Table 4.2: Analysis of variance of Signal to Noise (S/N) ratio

Source	DF	Seq SS	Adj SS	Adj MS	F	P	% Contribution
Alkali concentration	3	9.1165	9.1165	3.0388	22.82	0.014	51.80
Acid concentration	3	0.4586	0.4586	0.1529	1.15	0.456	2.61
L/S ratio	3	2.1072	2.1072	0.7024	5.27	0.103	11.96
Temperature	3	5.9157	5.9157	1.9719	14.81	0.026	33.62
Residual Error	3	0.3995	0.3995	0.1332			
Total	15	17.9975			44.05		100

$$S = 1.720606 \quad R\text{-Sq} = 97.97\% \quad R\text{-Sq}(\text{adj}) = 89.86\%$$

4.1.2 Residual Plots

Whether the proposed model fits the assumptions of the analysis or not, can be determined by the residual plot analysis. All the four residual plots are displayed in a single graph for the sake of comparing the plot trends to numerical measures

. The residual plots in the graph include:

- The relationship between residuals and fitted values which is a measure of constant variance. Any kind of nonlinearity, if obtained, can be inferred easily from this plot.
- Histogram representing skewed values and outliers, if available.
- Plot showing normal distribution of the data gives sufficient information about whether the response gets affected or not.
- The orderly effects in the data are indicated by residuals versus order of the data plot.

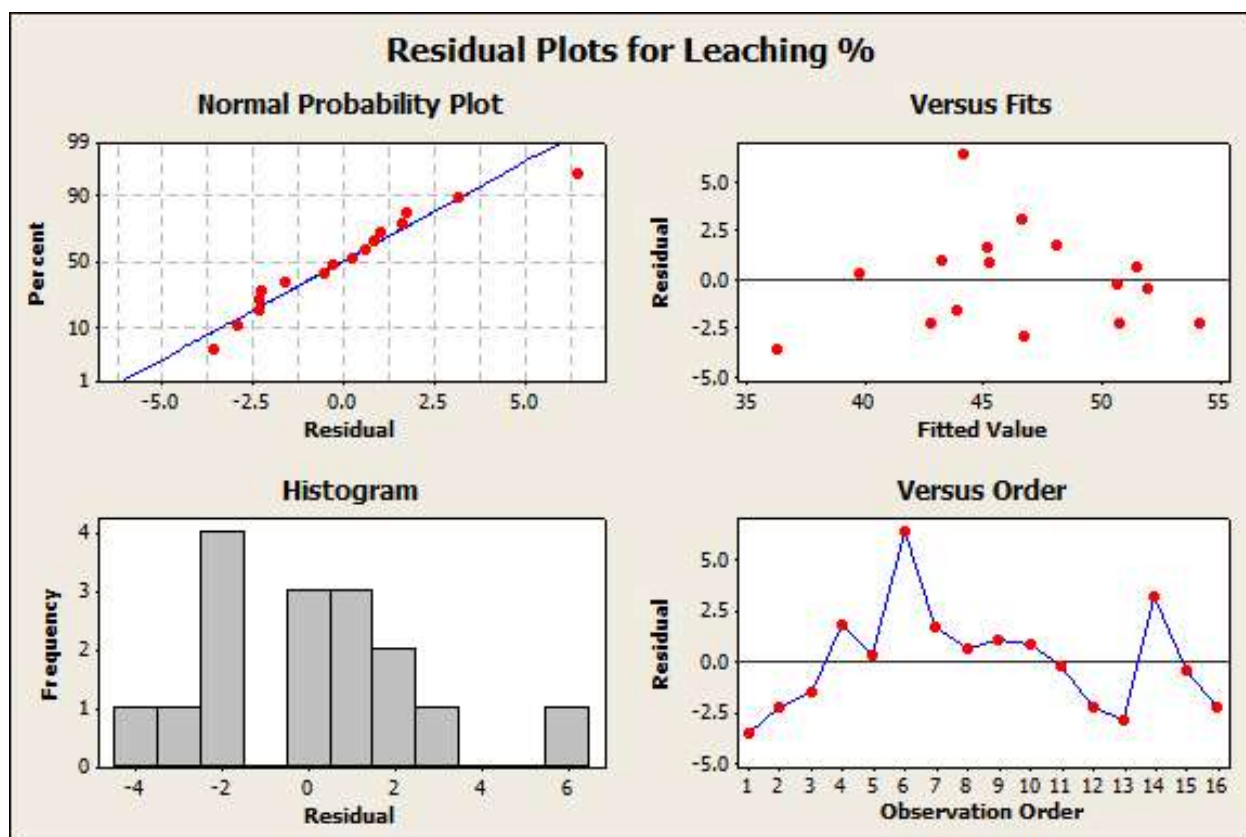


Figure 4.2: Four in one residual plot for leaching percentage of HNO_3 treatment.

Figure 4.2 drew a conclusion towards the normal distribution of residuals. The assumption of normality can be considered as apt as the residuals were mostly lying on a straight line. By the correlation between calculated and experimental values the sufficiency of ANOVA model was also tested. Residual and fitted values were presented in the scattered plot. An arbitrary, asymmetrical pattern was exhibited by the standardized residuals as inferred from the residual versus observation order plot. It is evident that the set of data obtained after experiment were decently on arbitrary basis with the residual data following no special pattern. This also confirms that the data were not interdependent.

4.2 SEM-EDX AND ULTIMATE ANALYSIS

The SPL particles obtained after passing through a 52 BSS screen can be said to have two parts. One is carbonaceous and the other one being inorganic materials of specific size fractions whose surfaces are prone to the atmosphere. The inner layers of graphene and bath materials

breaks resulting in the division of the above mentioned two parts^{2,30,46-48}. Figure 4.3 and 4.5 gave a clear representation that the fractional mineral discharge or exposure of the inorganic content from the carbon segment became prominent to a significantly great extent leading to better leach ability. Taking a close look at Figure 4.3 (i and ii), it can be observed that few extended graphite particles (dark in color) appeared entirely visible at this size fraction. When further magnification was done distinct inorganic (brighter colored) particles could be seen attached to the graphite counterparts not so firmly. Partially emerged graphite fractions became more visible in Fig. 4.3 (iii). Most of the inorganic fractions form a relatively thin layer that remained attached to graphite particles. The extent of leaching depends on the accessibility of these inorganic segments. It was observed that the structures which look like sharp needles are comprised of inorganic fractions. The appearance of inorganic fractions gradually became less significant due to removal of leachable fractions leading to dull garphitic particles present in the materials (Figure 4.3, 4.4, 4.5 and 4.6). The ultimate analysis was done for the SPL samples and results are included in the Table 4.3.

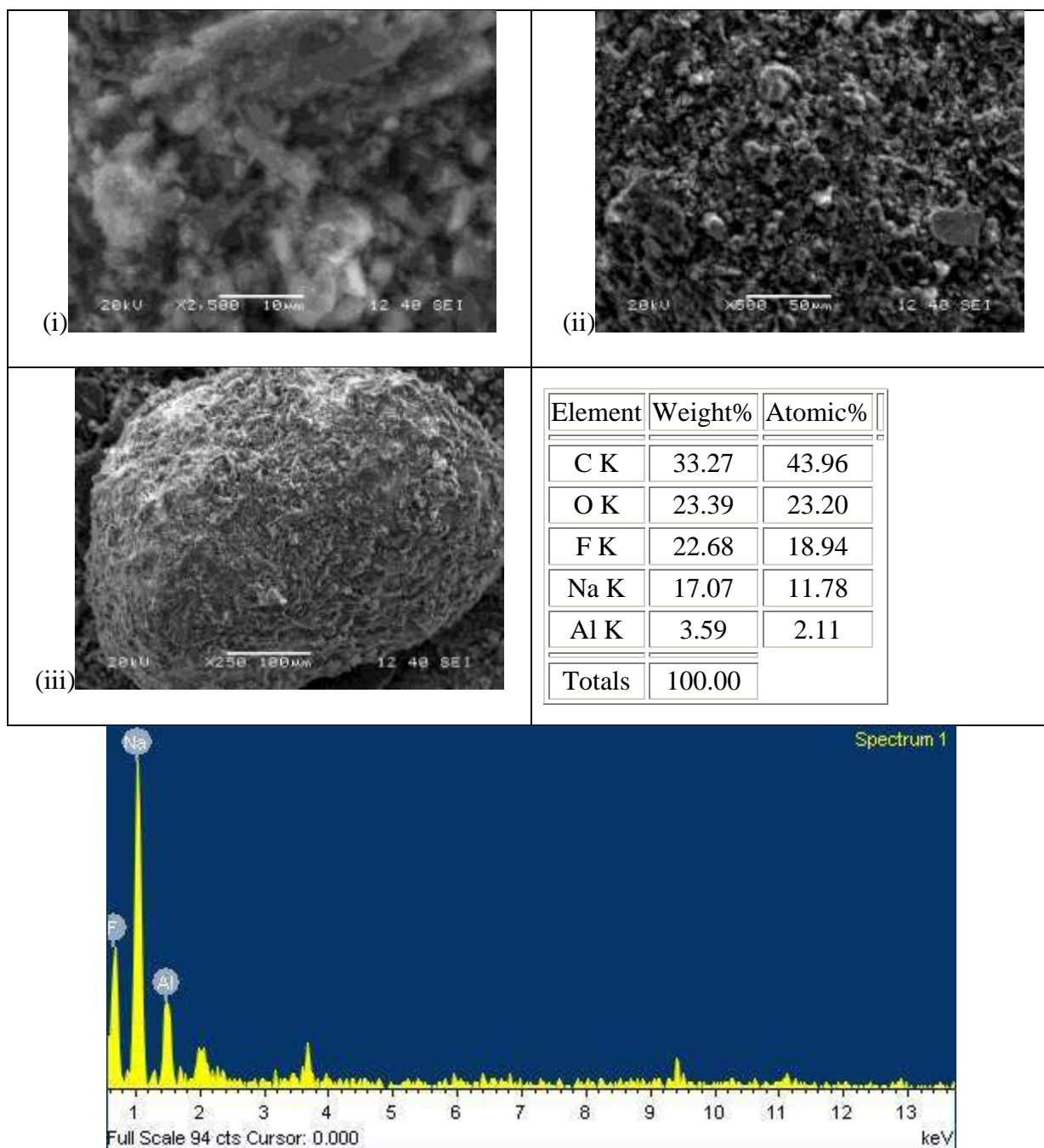


Figure 4.3: SEM-EDX images of Raw SPL, of magnification 10 μm, 50 μm, and 100 μm. (i, ii & iii)

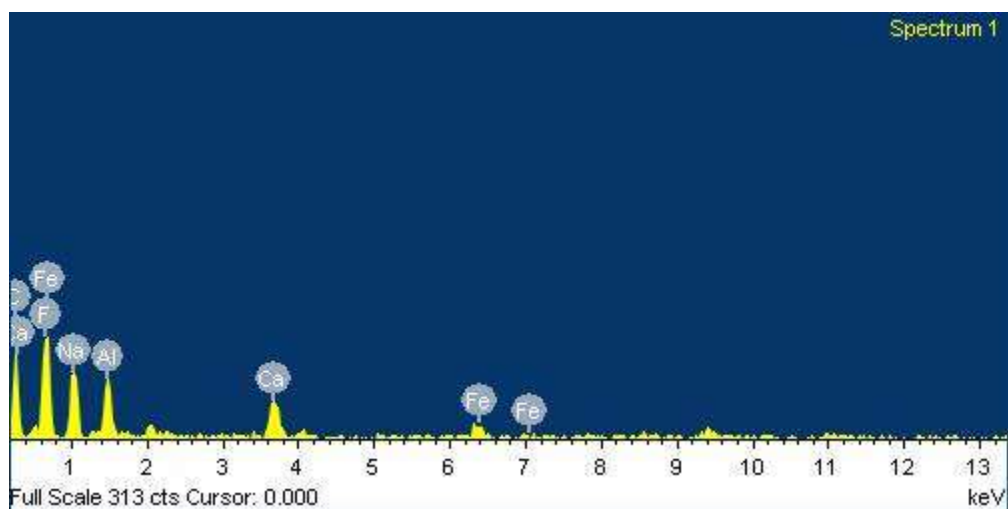
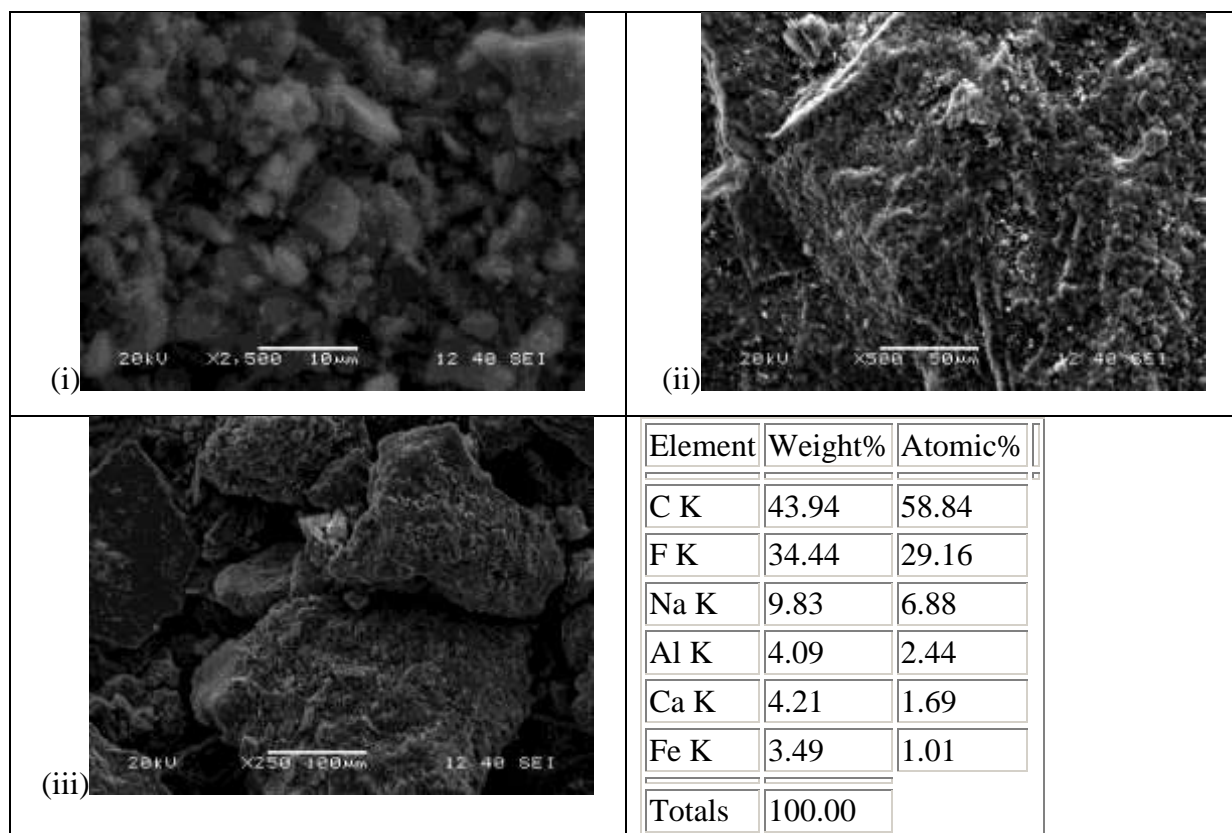


Figure 4.4: SEM images water washed SPL sample of magnification 10 μm , 50 μm , and 100 μm . (i, ii & iii)

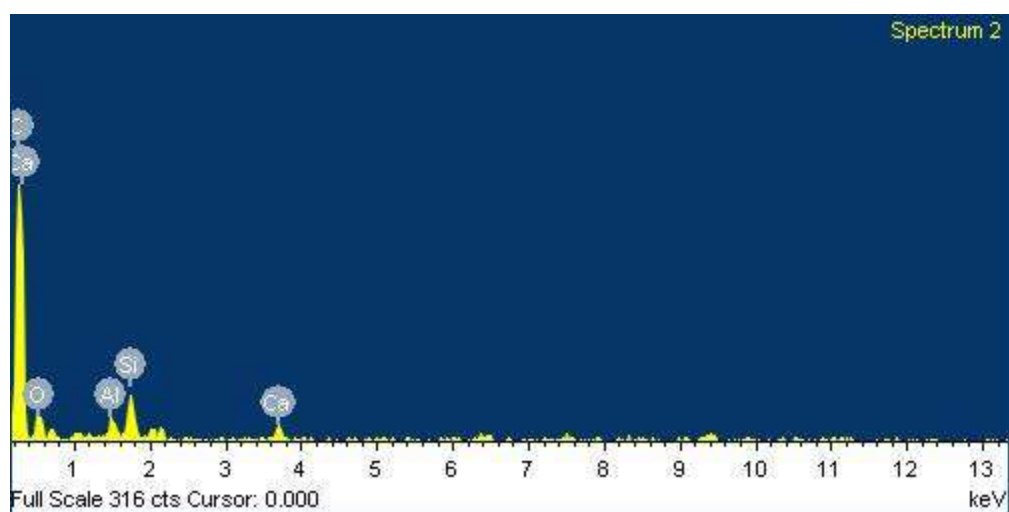
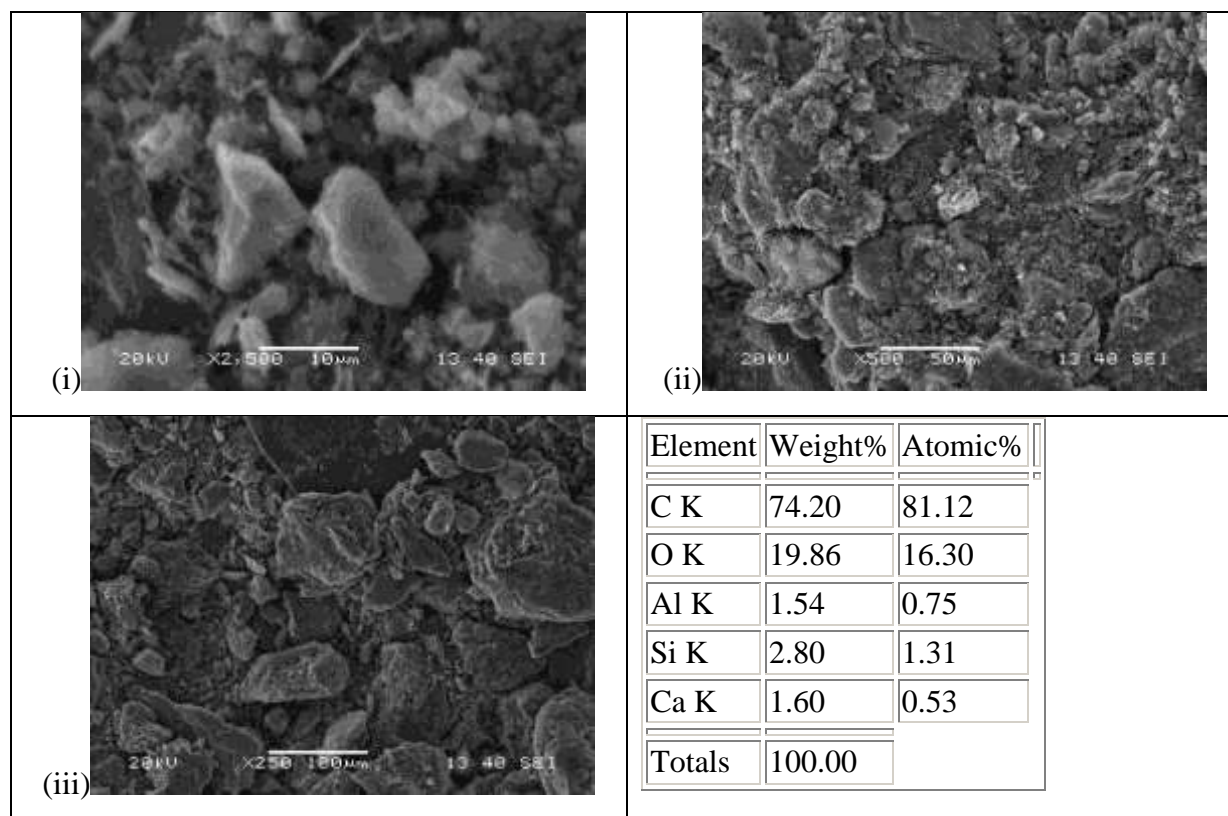


Figure 4.5: SEM-EDX images of alkali treated SPL at magnification 10 μm , 50 μm , and 100 μm at 1.5M NaOH concentration (i, ii, iii)

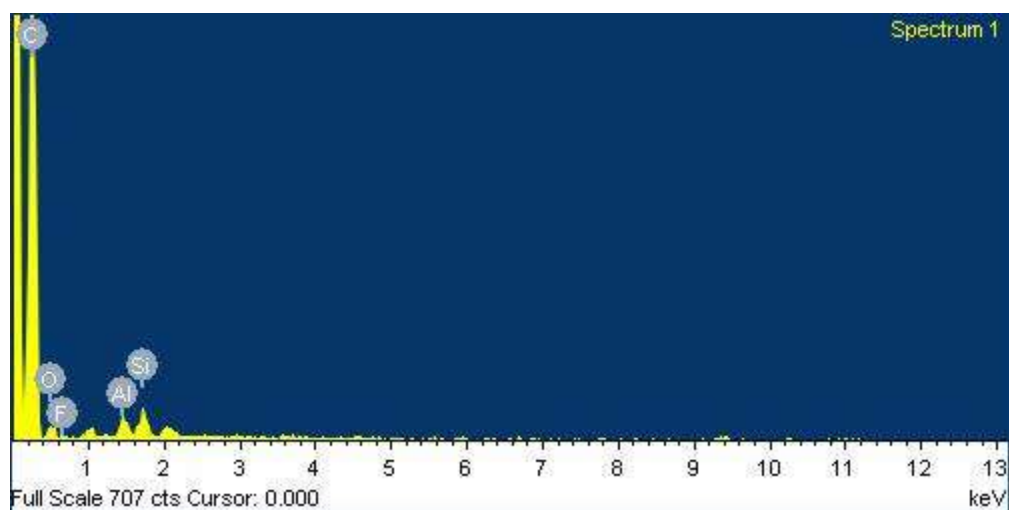
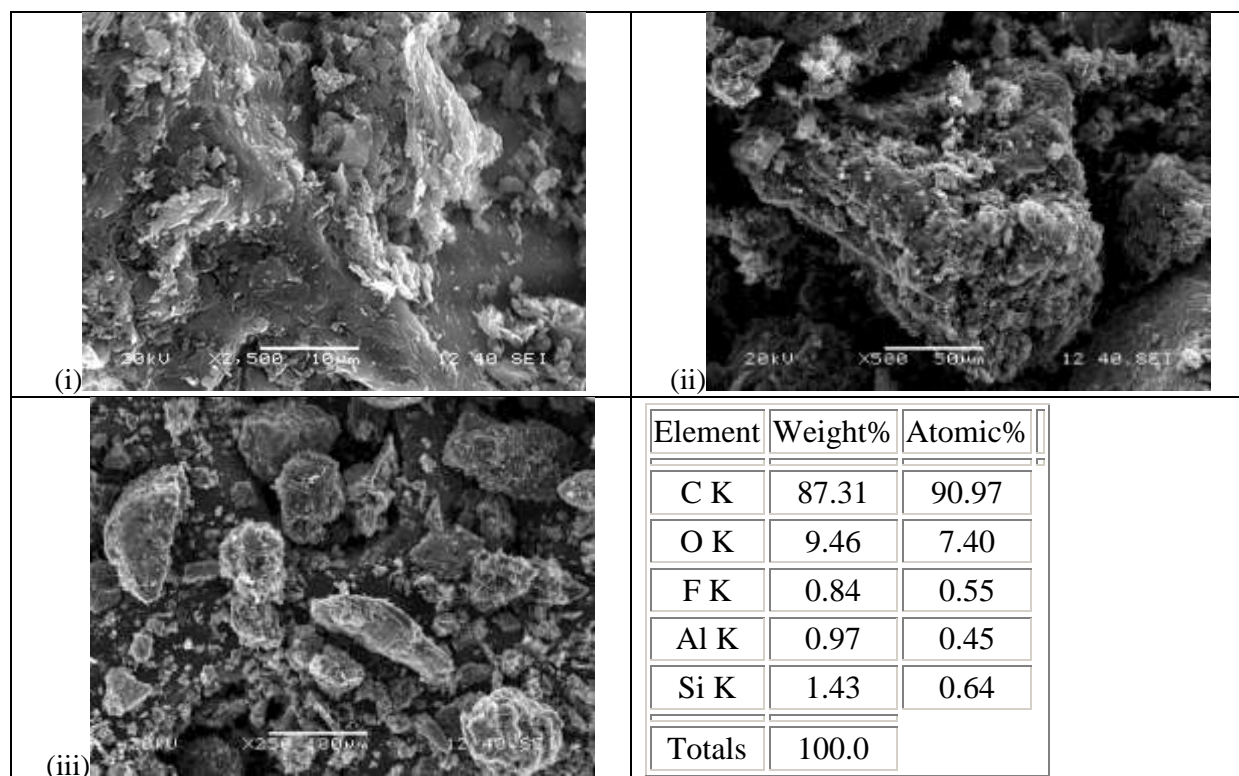


Figure 4.6: SEM-EDX images of the final treated SPL of magnification 10 μm , 50 μm , and 100 μm (i, ii & iii)

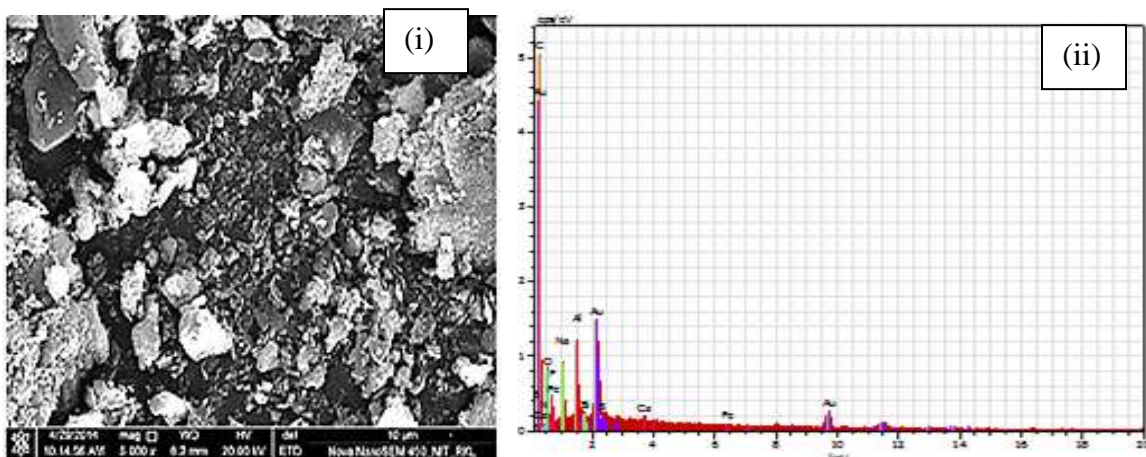


Figure 4.7: FESEM-EDX images of raw SPL (i, ii)

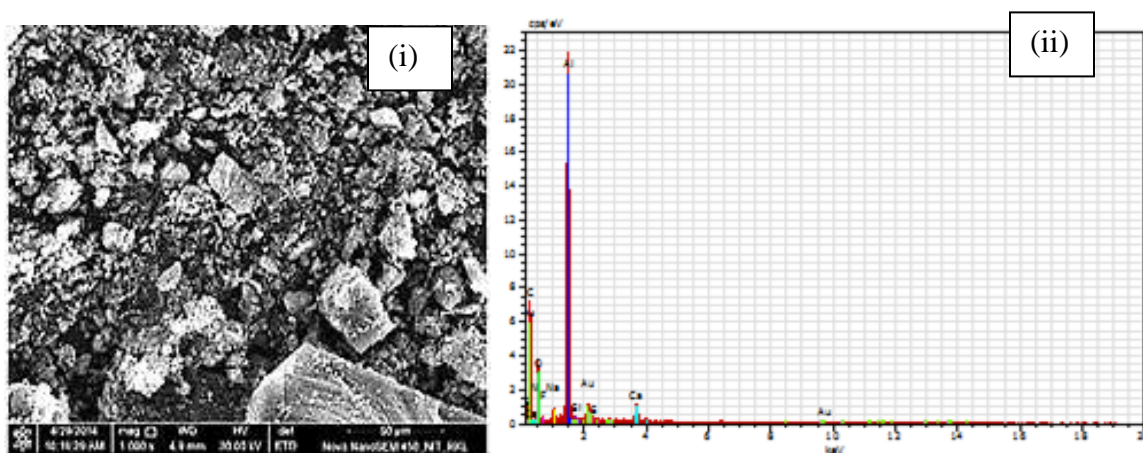


Figure 4.8: FESEM-EDX images of 2.5M NaOH treated SPL (i, ii)

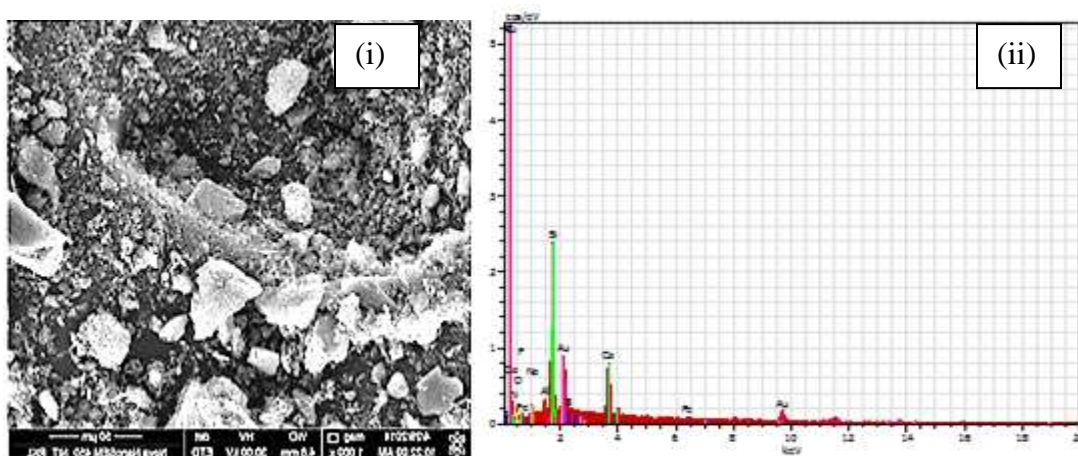


Figure 4.9: FESEM-EDX images of Final HNO₃ treated SPL(i, ii)

4.2.1 Elemental composition

Using CHNS analyzer the elemental compositions of the different treated SPL samples were found out. The purpose was to establish the occurrence of the heteroatom composition in each fraction which was being removed or enriched after treatment of SPL with the acid. The determination of hydrogen (H_2) to carbon (C) ratio of every fraction is a sign of the aromaticity and the predicted H_2 reduction amid SPL leaching. From the Table 4.3 it was concluded that the aromaticity has less prominent effect with a rise in concentration of acid. Yet the heteroatom compositions were augmented by the treatment of acid due to increase in sulfur content. However, no such trend in increment in other components was observed. Again the carbon content was found to increase from 43.39% (raw SPL) to 70.44% (HNO_3 treated SPL). The other parameters were kept constant for the acids (i.e. 10 M acid concentrations, 4.5 L/S ratio and temperature 100 °C).

Table 4.3: CHNS analysis of SPL samples

Component	Weight percentage (%)						
	C	H	N	S	H/C	N/C	S/C
Raw SPL	43.39	0.626	0.59	1.27	0.0146	0.013984	0.029391
Water Washed SPL	48.18	0.25	0.42	1.71	0.00435	0.008318	0.035769
5 M HNO_3 treated SPL	77.24	0.22	0.61	2.47	0.00416	0.008872	0.040302
10 M HNO_3 treated SPL	78.03	0.18	0.49	3.43	0.00269	0.007132	0.046754

4.2.2 X-ray diffraction (XRD) analysis

XRD analysis of final treated sample, the water washed sample and the raw sample was conducted. The peaks representing the intensity of graphitic carbon (C), cryolite (Na_3AlF_6), villaumite (NaF), fluorite (CaF_2), sodium iron cyanide ($\text{Na}_4\text{Fe}(\text{CN})_6$) and gibbsite ($\text{Al}(\text{OH})_3$) phases were obtained. The carbon peak can easily be seen to be higher in the final treated sample. Once alkali treated SPL was washed and filtered, the remaining solid residue obtained was found to be comprised of insoluble compounds of CaF_2 , $\text{Al}(\text{OH})_3$ and $\text{NaAl}_{11}\text{O}_{17}$ which is shown in Figure 4.10

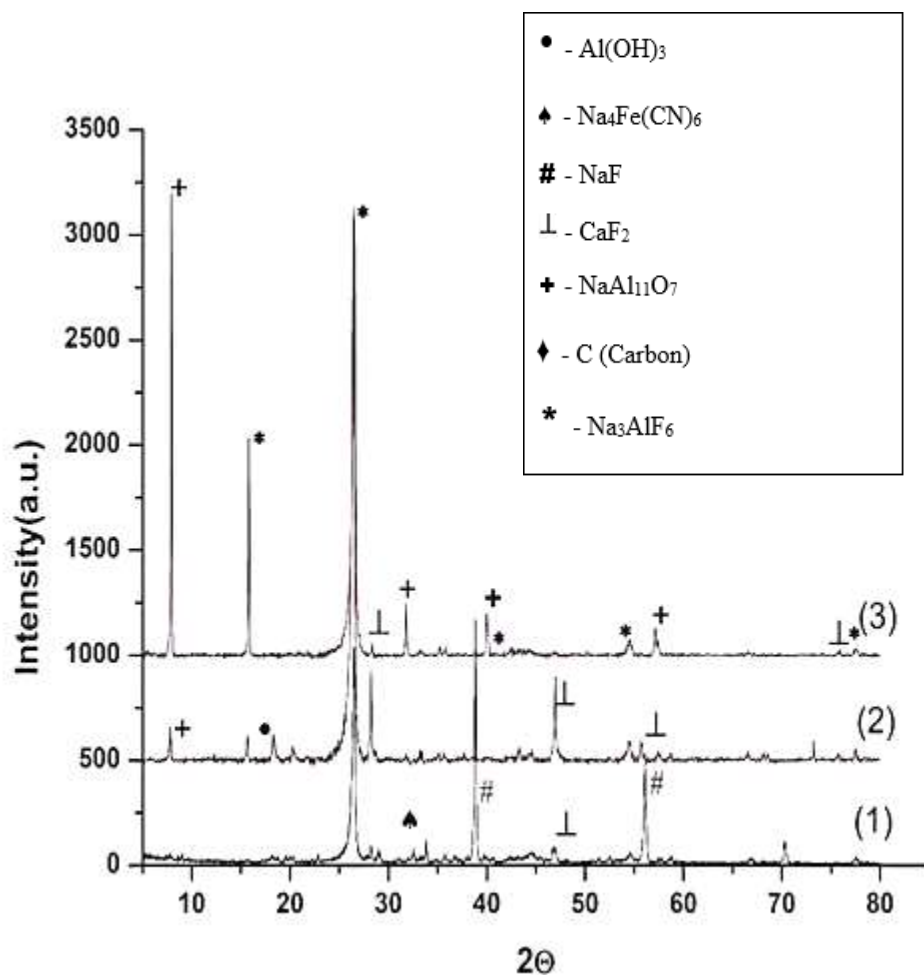


Figure 4.10: XRD analysis of SPL samples

4.3. COMPARISON OF LEACHABILITY OF VARIOUS ACIDS

From Fisher test it was predicted that out of all experimental parameters alkali concentration contributes the most towards finding the optimum leaching percentage. So an extensive comparison was made to find out the best suitable acid keeping the acid concentration and L/S ratio constant. Dependency of leaching percentage on alkali concentration for different acids such as HCl, HNO₃, H₂SO₄, HClO₄⁴⁶ at different temperatures was shown in Fig. 4.11, 4.12, 4.13 & 4.14.

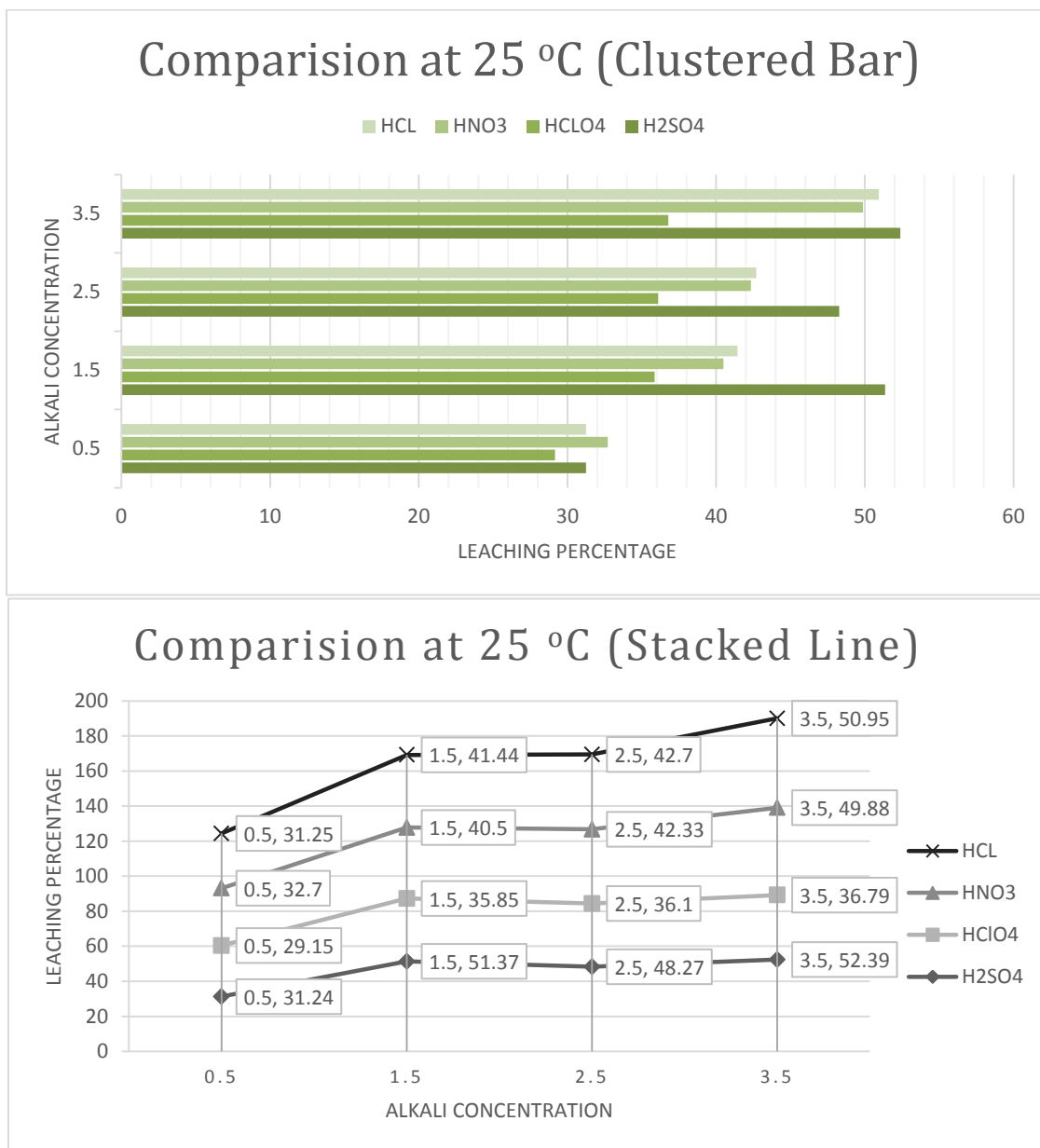


Figure 4.11: Comparison of leaching percentage using HCl, HNO₃, H₂SO₄, HClO₄ at 25 °C

a)Clustered Bar graph b)Stacked Line graph

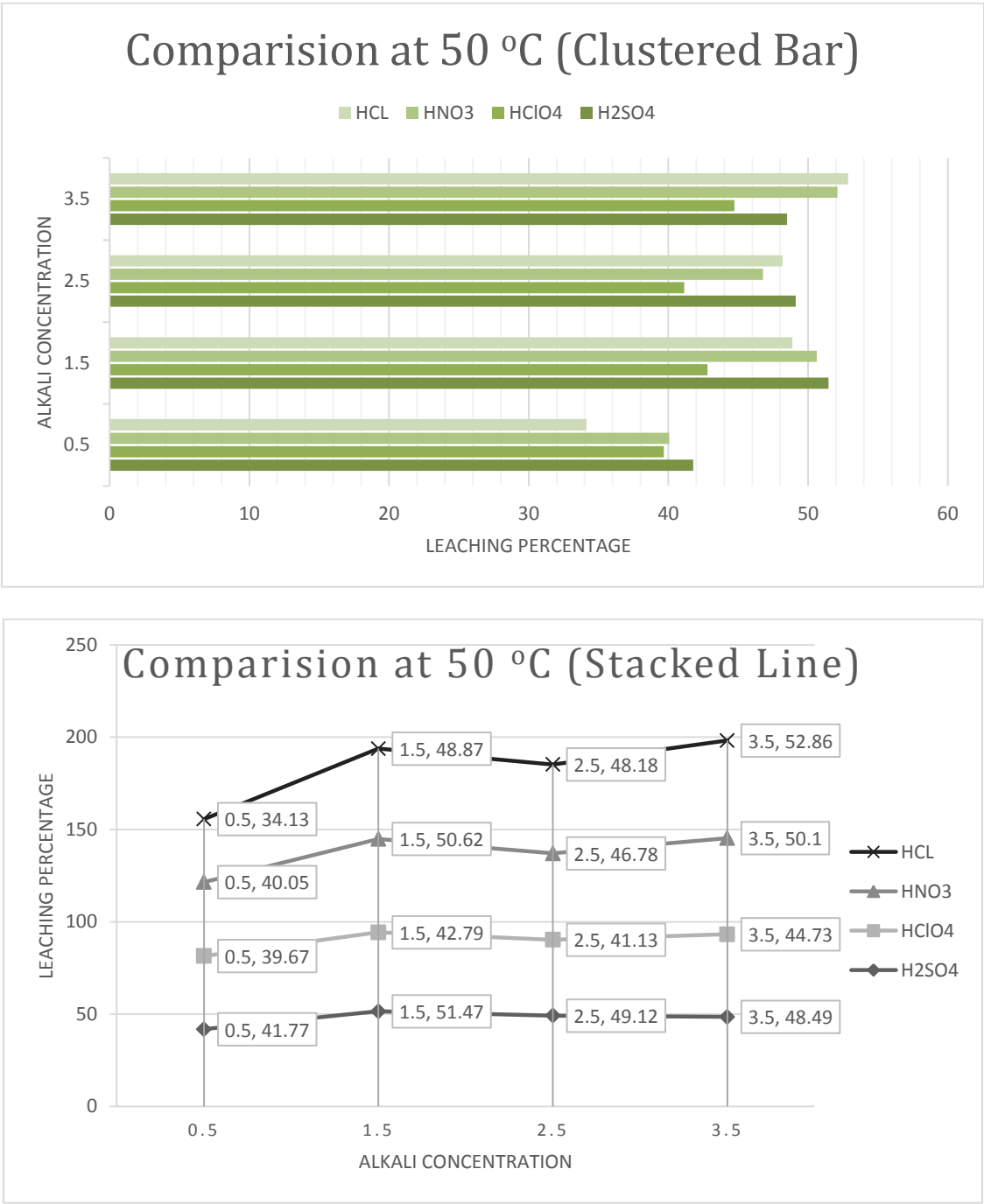


Figure 4.12: Comparison of leaching percentage using HCl, HNO₃, H₂SO₄, HClO₄ at 50 °C

a)Clustered Bar graph b)Stacked Line graph

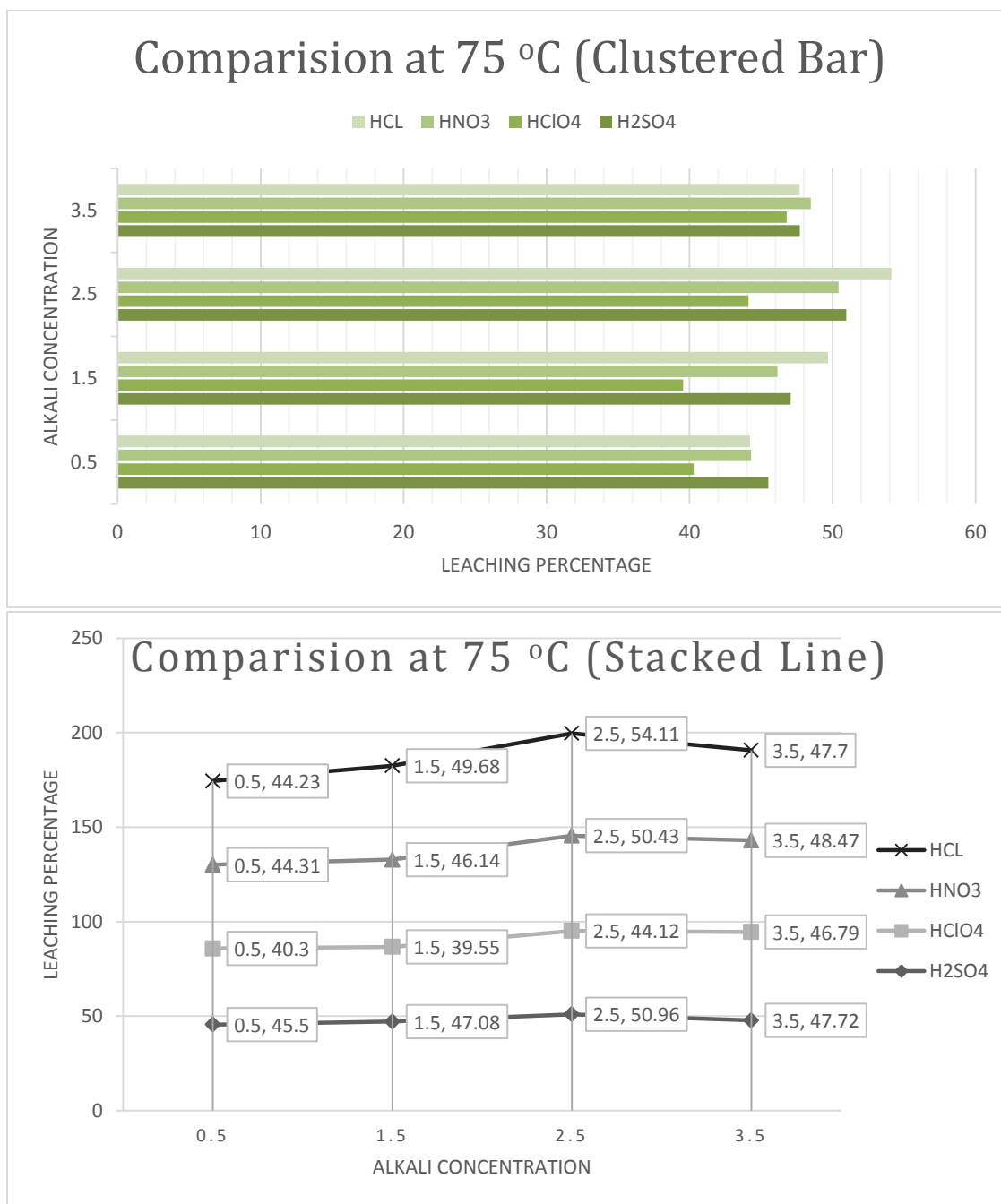


Figure 4.13: Comparison of leaching percentage using HCl, HNO₃, H₂SO₄, HClO₄ at 75 °C

a) Clustered Bar graph b) Stacked Line graph

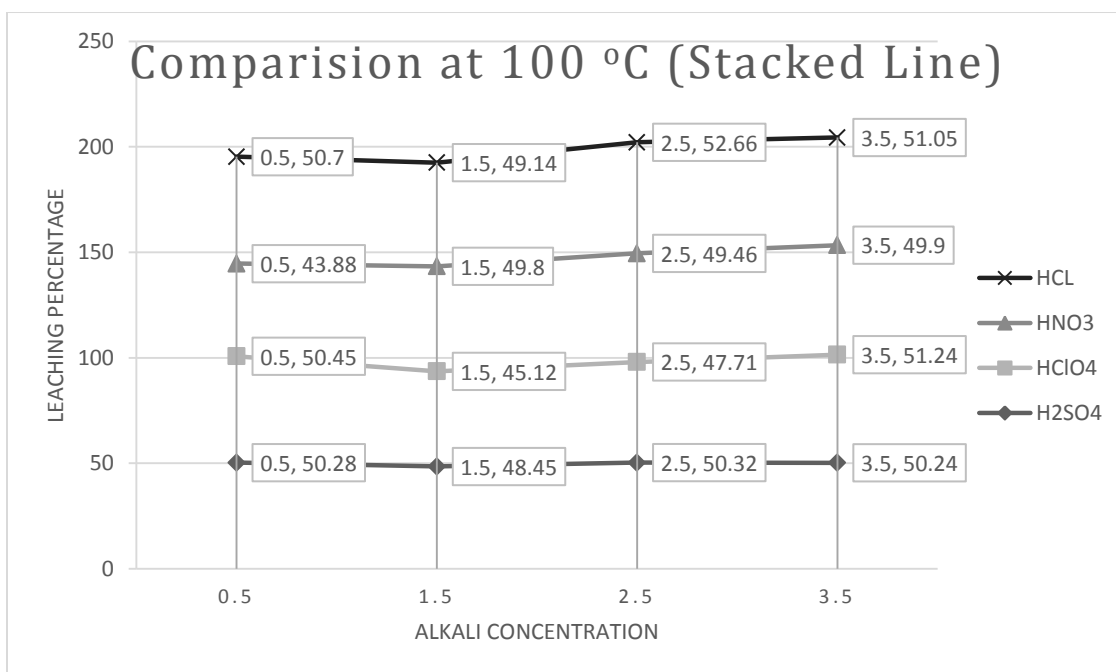
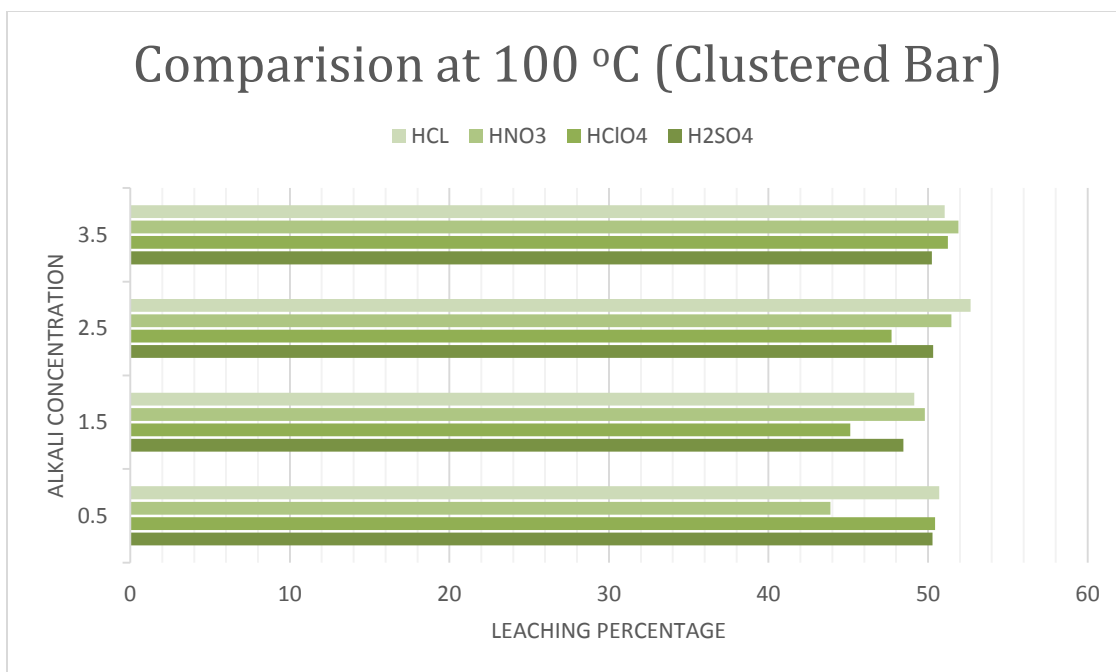
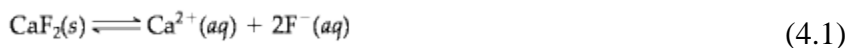


Figure 4.14: Comparison of leaching percentage using HCl, HNO₃, H₂SO₄, HClO₄ at 100 °C

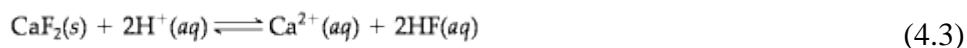
a)Clustered Bar graph b)Stacked Line graph

Fluorides being the most abundant complexes in SPL, leaching essentially meant dissolution of metallic fluorides (Na_3AlF_6 , NaF , CaF_2) and metals like Sodium, Calcium and Aluminium. Metal fluorides have similarities with other metal halides but are more ionic. Fluorides are more similar to oxides (Al_2O_3), often having similar bonding and crystal structures. The metals in an oxidation state of +3 or lower tend to form ionic refractory fluorides. The solubility of fluorides varies greatly but tends to increase as the charge on the metal ion decreases. So, fluorides of sodium, calcium etc form highly ionic compounds who have a high solubility in solutions having a higher H^+ content.⁴⁷

The solubility of CaF_2 increases as the solution becomes strongly acidic (higher pH), because the F^- ion is a weak base; it is the conjugate base of the weak acid HF. As a result, the solubility equilibrium of CaF_2 is shifted to the right as the concentration of F^- ions is reduced by protonation to form HF, or is used up by other available metal ions to form stable complexes. Thus, the solution process can be understood in terms of two consecutive reactions⁴⁸:



The equation for the overall process is:



The fluoride solubility in treatment of SPL involves the formation of AlF_i complexes from dissolving Na_3AlF_6 and CaF_2 solid phases. The dissolution of these complexes further drives the dissolution equilibria by attaching available fluorides to form complexes. The solubility of fluorides increased from 25 °C to 100 °C due to the increased stability of AlF_3 and AlF_4^- complexes with increasing temperature, so majority of the available dissociated fluorides (F^-) get used up. The increase in fluoride solubility as temperature was mostly due to CaF_2 solubilisation, as it can be seen by the overall increase in calcium solubility.^{28, 29}

Solution speciation models have been constructed for a broad range of mixed electrolyte aqueous solutions in numerous chemical and geochemical systems of environmental and industrial importance to predict the effect of influencing factors such as temperature, pH, or the concentration of ionic species.²⁹

4.4 CONCLUSIONS

- Alkali concentration was found to be the most significant factor amongst all the parameters. However, the L/S ratio and acid concentration were less significant amongst the four parameters studied.
- Alkali concentration contributed 51.80% in the leaching process, whereas acid concentration contributed only 2.61 %. The maximum leaching percentage was found out to be 50.62% by Taguchi optimization.
- From the S/N ratio analysis and leaching percentage obtained two possible optimum conditions can be proposed. One was attained at 1.5 M NaOH concentration, 10 M HNO₃ concentration and 3.5 L/S ratio at 50 ±1°C. The other combination of experimental parameters was 2.5 M NaOH concentration, 5 M HNO₃ concentration and 4.5 L/S ratio at 75 ±1°C. But from the Fisher test it was known that HNO₃ concentration has a lesser percentage contribution as compared to temperature. So it was concluded that 2.5 M NaOH concentration, 5 M HNO₃ concentration, 4.5 L/S ratio and temperature 75 ±1°C was the best combination for the optimum leaching percentage for “final treated SPL”.
- The carbon percentage (weight %) of SPL was increased from 33.27% to 87.31% as confirmed from the elemental composition obtained by Energy Dispersive X-ray spectroscopy. From the CHNS analysis, the carbon percentage was found to be increased from 43.39% to 78.03% from the raw to final treated SPL.
- From the comparison of various acids it is observed that at normal temperatures H₂SO₄ gave maximum leaching percentage for all values of alkali concentrations. But as temperature was increased from 25°C to 100°C, the leaching percentage obtained by all acids converged slowly to a constant range. At 100°C all four acids (HCl, HNO₃, H₂SO₄ & HClO₄) irrespective of the alkali concentration gave rise to an almost same value of leaching percentage.
- A combination of two factors, Alkali concentration (because of its high reactivity with the compounds present in SPL) and temperature (because of its favorability in stabilizing the complex formed during fluoride/metal solubility) gave the best results in leaching.

CHAPTER 5:

FUTURE WORK

5.1 FUTURE RECOMMENDATIONS:

- Further acidic leaching can be done using various tribasic and dibasic acids to carry forward the comparative analysis.
- The potential of final treated SPL for using as ramming paste for the cathode lining can be studied. Again in aluminum industries it can be used as green anode, but the viability of this can be checked on a laboratory scale.
- The filtrate obtained after water washing can be used for blending purpose to maintain the cryolite ratio.
- A set of model equations can be developed for predicting the calorific value by the use of multiple linear regression of ultimate and proximate analysis.

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